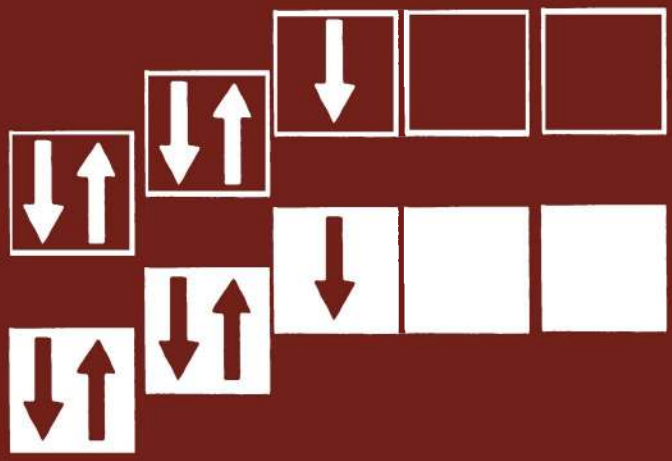
E.T. OGANESIAN

CHEMISTRY
A REFRESHER COURSE



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PERIODIC TABLE

		Groups of				
		I	II	III	IV	V
1	I	**H** 1 1.0079 $1s^1$ 1 Hydrogen				
2	II	**Li** 3 6.941 $2s^1$ 1 2 Lithium	**Be** 4 9.01218 $2s^2$ 2 2 Beryllium	**B** 5 10.81 3 $2p^1$ 2 Boron	**C** 6 12.011 4 $2p^2$ 2 Carbon	**N** 7 14.0067 5 $2p^3$ 2 Nitrogen
3	III	**Na** 11 22.98977 $3s^1$ 1 8 2 Sodium	**Mg** 12 24.305 $3s^2$ 2 8 2 Magnesium	**Al** 13 26.98154 3 $3p^1$ 8 2 2 Aluminium	**Si** 14 28.0855 4 $3p^2$ 8 2 2 Silicon	**P** 15 30.97376 5 $3p^3$ 8 2 2 Phosphorus
4	IV	**K** 19 39.0983 $4s^1$ 1 8 8 2 Potassium	**Ca** 20 40.08 $4s^2$ 2 8 8 2 Calcium	**Sc** 21 44.9559 $3d^14s^2$ 2 9 8 2 Scandium	**Ti** 22 47.90 $3d^24s^2$ 2 10 8 2 Titanium	**V** 23 50.9415 $3d^34s^2$ 2 11 8 2 Vanadium
	V	**29 Cu** 63.546 1 18 8 2 $3d^{10}4s^1$ Copper	**30 Zn** 65.38 2 18 8 $4s^2$ 2 Zinc	**31 Ga** 69.72 3 18 8 $4p^1$ 2 Gallium	**32 Ge** 72.59 4 18 8 $4p^2$ 2 Germanium	**33 As** 74.9216 5 18 8 $4p^3$ 2 Arsenic
5	VI	**Rb** 37 85.4678 $5s^1$ 1 8 18 8 2 Rubidium	**Sr** 38 87.62 $5s^2$ 2 8 18 8 2 Strontium	**Y** 39 88.9059 $4d^15s^2$ 2 9 18 8 2 Yttrium	**Zr** 40 91.22 $4d^25s^2$ 2 10 18 8 2 Zirconium	**Nb** 41 92.9064 $4d^45s^1$ 1 12 18 8 2 Niobium
	VII	**47 Ag** 107.8682 1 18 18 $5s^1$ 8 2 Silver	**48 Cd** 112.41 2 18 18 $5s^2$ 8 2 Cadmium	**49 In** 114.82 3 18 18 $5p^1$ 8 2 Indium	**50 Sn** 118.69 4 18 18 $5p^2$ 8 2 Tin	**51 Sb** 121.75 5 18 18 $5p^3$ 8 2 Antimony
6	VIII	**Cs** 55 132.9054 $6s^1$ 1 8 18 18 8 2 Cesium	**Ba** 56 137.33 $6s^2$ 2 8 18 18 8 2 Barium	**57La-Lu71** *	**Hf** 72 178.49 $5d^26s^2$ 2 10 32 18 8 2 Hafnium	**Ta** 73 180.9479 $5d^36s^2$ 2 11 32 18 8 2 Tantalum
	IX	**79 Au** 196.9665 1 18 32 18 $5d^{10}6s^1$ 8 2 Gold	**80 Hg** 200.59 2 18 32 18 $6s^2$ 8 2 Mercury	**81 Tl** 204.37 3 18 32 18 $6p^1$ 8 2 Thallium	**82 Pb** 207.2 4 18 32 18 $6p^2$ 8 2 Lead	**83 Bi** 208.9804 5 18 32 18 $6p^3$ 8 2 Bismuth
7	X	**Fr** 87 [223] $7s^1$ 1 8 18 32 18 8 2 Francium	**Ra** 88 226.0254 $7s^2$ 2 8 18 32 18 8 2 Radium	**89 103** **Ac-(Lr)** **	**Ku** 104 [261] $6d^27s^2$ 2 10 32 32 18 8 2 Kurchatovium	**Ns** 105 [261] $6d^37s^2$ 2 11 32 32 18 8 2 Nielsborium

* LANTHANOIDS

La 57 138.9055 $5d^16s^2$ 2 8 18 18 9 2 Lanthanum	**Ce** 58 140.12 $4f^26s^2$ 2 8 20 18 8 2 Cerium	**Pr** 59 140.9077 $4f^36s^2$ 2 8 21 18 8 2 Praseodymium	**Nd** 60 144.24 $4f^46s^2$ 2 8 22 18 8 2 Neodymium	**Pm** 61 [145] $4f^56s^2$ 2 8 23 18 8 2 Promethium	**Sm** 62 150.4 $4f^66s^2$ 2 8 24 18 8 2 Samarium	**Eu** 63 151.965 $4f^76s^2$ 2 8 25 18 8 2 Europium	**Gd** 64 157.2 $4f^75d^16s^2$ 2 9 25 18 8 2 Gadolinium

** ACTINOIDS

Ac 89 [227] $6d^17s^2$ 2 8 18 32 18 9 2 Actinium	**Th** 90 232.0381 $6d^27s^2$ 2 8 18 32 18 10 2 Thorium	**Pa** 91 231.0359 $5f^26d^17s^2$ 2 8 20 32 18 9 2 Protactinium	**U** 92 238.029 $5f^36d^17s^2$ 2 8 21 32 18 9 2 Uranium	**Np** 93 237.0482 $5f^46d^17s^2$ 2 8 22 32 18 9 2 Neptunium	**Pu** 94 [244] $5f^67s^2$ 2 8 24 32 18 8 2 Plutonium	**Am** 95 [243] $5f^77s^2$ 2 8 25 32 18 8 2 Americium	**Cm** 96 [247] $5f^76d^17s^2$ 2 9 25 32 18 8 2 Curium

OF THE ELEMENTS

elements

VI	VII	VIII		
	H			2 He 4.00260 $1s^2$ Helium
8 O 15.999$_4$ $2p^4$ Oxygen	9 F 18.998403 $2p^5$ Fluorine			10 Ne 20.179 $2p^6$ Neon
16 S 32.06 $3p^4$ Sulphur	17 Cl 35.453 $3p^5$ Chlorine			18 Ar 39.948 $3p^6$ Argon
Cr 24 51.996 $3d^5 4s^1$ Chromium	Mn 25 54.9380 $3d^5 4s^2$ Manganese	Fe 26 55.847 $3d^6 4s^2$ Iron	Co 27 58.9332 $3d^7 4s^2$ Cobalt	Ni 28 58.70 $3d^8 4s^2$ Nickel
34 Se 78.96 $4p^4$ Selenium	35 Br 79.904 $4p^5$ Bromine			36 Kr 83.80 $4p^6$ Krypton
Mo 42 95.94 $4d^5 5s^1$ Molybdenum	Tc 43 98.9062 $4d^5 5s^2$ Technetium	Ru 44 101.07 $4d^7 5s^1$ Ruthenium	Rh 45 102.9055 $4d^8 5s^1$ Rhodium	Pd 46 106.4 $4d^{10} 5s^0$ Palladium
52 Te 127.60 $5p^4$ Tellurium	53 I 126.9045 $5p^5$ Iodine			54 Xe 131.30 $5p^6$ Xenon
W 74 183.85 $5d^4 6s^2$ Tungsten	Re 75 186.207 $5d^5 6s^2$ Rhenium	Os 76 190.2 $5d^6 6s^2$ Osmium	Ir 77 192.22 $5d^7 6s^2$ Iridium	Pt 78 195.09 $5d^9 6s^1$ Platinum
84 Po [209] $6p^4$ Polonium	85 At [210] $6p^5$ Astatine			86 Rn [222] $6p^6$ Radon

Atomic mass — Atomic number

U 92 — Distribution of electrons by levels

238.029 — $5f^3 6d^1 7s^2$ — Uranium

Distribution of electrons by unfilled and following completed sublevels

Atomic masses are given from the International Table of 1981. The accuracy of the last significant digit is ±1 or ±3 if set in small type. The numbers in brackets are the mass numbers of the most stable isotopes. The names and symbols of elements in parentheses are not generally adopted.

Tb 65 158.9254 $4f^9 6s^2$ Terbium	Dy 66 162.50 $4f^{10} 6s^2$ Dysprosium	Ho 67 164.9304 $4f^{11} 6s^2$ Holmium	Er 68 167.26 $4f^{12} 6s^2$ Erbium	Tm 69 168.9342 $4f^{13} 6s^2$ Thulium	Yb 70 173.04 $4f^{14} 6s^2$ Ytterbium	Lu 71 174.967 $5d^1 6s^2$ Lutetium
Bk 97 [247] $5f^9 6d^1 7s^2$ Berkelium	Cf 98 [251] $5f^{10} 7s^2$ Californium	Es 99 [254] $5f^{11} 7s^2$ Einsteinium	Fm 100 [257] $5f^{12} 7s^2$ Fermium	Md 101 [258] $5f^{13} 7s^2$ Mendelevium	(No) 102 [255] $5f^{14} 7s^2$ (Nobelium)	(Lr) 103 [256] $6d^1 7s^2$ (Lawrencium)

CHEMISTRY

A REFRESHER COURSE

Э. Т. ОГАНЕСЯН

РУКОВОДСТВО ПО ХИМИИ

ИЗДАТЕЛЬСТВО «ВЫСШАЯ ШКОЛА» МОСКВА

E.T. OGANESIAN

CHEMISTRY
A REFRESHER COURSE

Translated from the Russian
by G. Leib



MIR PUBLISHERS MOSCOW

First published 1989
Revised from the 1987 Russian edition

На английском языке

Printed in the Union of Soviet Socialist Republics

ISBN-5-03-000895-0

© Издательство «Высшая школа», 1987
© English translation, Mir Publishers, 1989

PREFACE

The present book is intended as a refresher course in chemistry for students preparing for their entrance examinations to higher educational institutions.

The difficulties experienced by would-be college students when studying chemistry independently are due first of all to a lack of skill in applying their theoretical knowledge to generalization of the material being studied or to problem-solving.

My main objective in preparing this book was to set out the common theoretical concepts of general, inorganic, and organic chemistry in such a way as to provide the required level of knowledge for all the readers taking into account their various levels of mastering the subject.

The book consists of three parts. Part I treats the most important concepts, laws, and theoretical foundations of chemistry in accordance with the syllabus for secondary schools. Part II treats the chemistry of the elements, and Part III—the fundamentals of organic chemistry.

Each chapter starts with its objectives and ends in a summary. The chapters of Part I contain examples of solving typical problems. The questions and problems at the end of each section will help the reader evaluate his knowledge and facilitate mastering of the material. Answers to selected problems will be found at the end of the book.

A glossary is given in addition to the index. It will be useful for finding the most important definitions and concepts.

The book will also be an excellent aid for secondary school pupils preparing for their graduation examinations.

I am extremely grateful to V.I. Tsirelnikov and G.N. Fadeev for their valuable remarks and advice when reviewing the book, and to G.M. Chernobelskaya for her great aid in preparing the manuscript.

I will be glad to receive any suggestions and comments on this book from instructors and students.

Eduard T. Oganesian

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Part I

FUNDAMENTALS OF GENERAL CHEMISTRY

CHAPTER 1

IMPORTANT CONCEPTS IN CHEMISTRY

OBJECTIVES

To know the definition of the concepts "atom", "element", "molecule"; to be able to distinguish physical and chemical phenomena, determine the valence, relative atomic mass, and atomic ratio; to know the simplest and true formulas.

1.1. Theory of Atoms and Molecules

Chemistry is a science dealing with substances and the processes of their transformation attended by changes in their composition and structure.

Modern chemistry, on the one hand, involves the production of synthetic polymers and fibres, high-strength steels and anticorrosion materials, chemical fertilizers and means for protecting plants from a variety of pests, the refining of petroleum and gas, the production of highly effective drugs for use in medicine, and the development of means for protecting the environment.

On the other hand, modern chemistry involves comprehensive theoretical research into processes and phenomena that are the basis for developing progressive production processes and new materials, and for the development of new directions of the chemical science.

The science of chemistry is based on the theory of atoms and molecules, the law of conservation of matter, Mendeleev's periodic table, and the theory of chemical structure.

The theory of atoms and molecules developed at the end of the 18th and beginning of the 19th centuries, i.e. at the time when quantitative methods of research were introduced into chemistry. An enormous contribution to the creation of this theory was made by the Russian scientist M. Lomonosov. The fundamentals of this theory are as follows.

1. Substances consist of molecules; molecules of various substances differ in their chemical composition, size, physical and chemical properties.

2. Molecules are in continuous motion; mutual attraction and repulsion exist between them. The velocity of molecules depends on the state of aggregation of the substances they form.

3. In physical phenomena, the composition of molecules remains unchanged; in chemical phenomena, they experience qualitative and quantitative changes, and new molecules appear instead of the previous ones.

4. Molecules consist of atoms. The latter are characterized by a definite size and mass. The properties of the atoms of one element are identical and differ from those of the atoms of other elements.

Unlike molecules, in chemical reactions atoms experience no qualitative changes.

An atom is an electrically neutral particle consisting of a positively charged atomic nucleus and negatively charged electrons.

An atom is the tiniest particle preserving its identity in chemical changes.

Atoms can interact with one another to form molecules. Consequently, a molecule can be described as a system consisting of atoms bonded together. This system, as an integral entity, has a new set of properties.

A molecule is the smallest particle of a substance retaining its typical chemical properties.

A molecule can exist independently and consists of the same or different atoms joined together into an entity by chemical bonds.

Not any substance consists of molecules. Many substances with a nonmolecular structure are known including the noble gases and substances forming ionic or atomic crystals.

If a substance is formed by like atoms, it is said to be simple, while if it is formed by unlike atoms, it is said to be complex.

Questions and Problems

1. What relates the concepts "atom" and "molecule"? What is the difference between them?

2. Is the statement "A substance always consists of molecules" correct? Why?

3. In what does a simple substance differ from a complex one? What is the similarity between them?

1.2. A Chemical Element. Allotropy

A definite species of atoms with the same positive charge of the nucleus is called a chemical element.

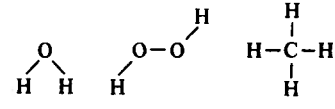
Consequently, the properties of all the atoms of one element are identical and differ from the properties of atoms of other elements. An atom is the carrier of the properties of a chemical element.

At present 110 chemical elements are known*, but only 92 of them are encountered in nature. The elements known as the noble gases usually occur in the form of isolated atoms.

Each chemical element is designated by a symbol that implies the species of the element and also stands for a single atom of it. For example, the symbol Cu designates one atom of copper, and H, one atom of hydrogen.

The composition of substances is shown by chemical formulas. The relevant symbols indicate the chemical elements contained in the substance, and the subscripts to the right of the symbols indicate the number of atoms of each element (the subscript "1" is omitted). For instance, a molecule of sulphuric acid H_2SO_4 contains two hydrogen atoms, one sulphur atom, and four oxygen atoms.

Chemical formulas showing the true number of atoms in a molecule are called **true** or **molecular formulas.** If a chemical formula indicates only the ratio of the atoms in a molecule, it is called a **simplest** or **empirical formula.** It shows the species of the atoms in a molecule and their ratio, e.g. CH. When writing formulas, the sequence of the mutual arrangement of the atoms in a molecule is often indicated. Such formulas are called **structural** ones. For example, the formulas of water, hydrogen peroxide, and methane can be depicted as follows:



Here each bond is designated by a single dash. It should be remembered that structural formulas do not always give an idea of the geometry of a molecule.

There is a distinction between the concepts of a simple substance and a chemical element. Any simple substance is characterized by a strictly definite set of features such as its colour, shape of its crystals (for crystalline substances), density, and boiling and melting points. Consequently, simple substances differ from one another in these and other features.

When speaking of the properties of a chemical element, on the other hand, one must remember that this implies the typical features of individual atoms, and first of all the charge of the nucleus.

For example, the difference between the simple substances O_2 (dioxygen) and O_3 (trioxygen or ozone) consists in the number of atoms in a molecule. Ozone under ordinary conditions decomposes into O_2 and O. Hence, the element oxygen in the free state can exist in the form of two simple substances—allotropic modifications.

---

* Isotopes of the elements numbered 108-110 were first obtained in 1982-1986 in the USSR.

The ability of a chemical element to form several simple substances is called allotropy.

Allotropy is due to several reasons, namely, (1) the formation of molecules with a different number of atoms (oxygen and ozone; diatomic phosphorus P_2 and tetratomic phosphorus P_4 with a molecule in the form of a regular tetrahedron, etc.), and (2) the formation of crystals of various modifications — a particular case of polymorphism (carbon in the form of graphite and diamond, the modifications of sulphur, etc.).

Over 400 allotropic modifications of simple substances are known.

Question and Problems

1. In what does a simple substance differ from an element? What do we have in view wher we speak of "a chemical element in the free state"?
2. What is the relation between the concepts of an atom and a chemical element?
3. Why is allotropy possible? What examples of allotropic modifications do you know?
4. One of the modifications of sulphur consists of lemon-yellow rhombic crystals. If the crystals are melted and then poured into cold water, an elastic rubber-like substance forms. When sulphur is heated with an iron powder, a homogeneous substance forms which when cooled transforms into iron sulphide. Which of these processes are physical or chemical and why? Does allotropy occur here?

1.3. Relative Atomic and Molecular Masses. Amount of Substance. The Mole. Valence. Constant Composition of Substances. Calculation by Chemical Formulas

A second important characteristic of an atom after the charge of its nucleus is its mass. The true mass of an atom of an element expressed in kilogrammes is called the **absolute atomic mass** (m_a). For instance, the mass of a carbon atom is 1.99×10^{-26} kg. But it is not convenient to express the masses of atoms in the SI unit of mass—the kilogramme—because very low values are obtained and this makes their use involved. This is why when calculating atomic masses, one-twelfth of the mass of a carbon isotope atom with a mass number of 12 is taken as the unit of mass. It is called the **atomic mass unit** (amu): $1 \text{ amu} = 1.667 \times 10^{-27}$ kg. It provides a single basis for chemical and physical calculations.

The mass of an atom expressed in atomic mass units is called the atomic weight or the relative atomic mass. It is a dimensionless quantity.

The relative atomic mass shows how many times the mass of an atom of a given element is heavier than one-twelfth of the mass of the carbon isotope $^{12}_{6}C$. The relative atomic mass of iron is 56. This signifies that the iron atom ^{56}Fe is 56 times heavier than one-twelfth of the mass of a carbon atom.

The relative mass is designated by A_r, and the absolute mass, by m_a. They are related by the formula $m_a = A_r \times 1$ amu.

Molecules can be described by using the corresponding concepts of the absolute (m_m) and relative (M_r) molecular mass.

The molecular weight or relative molecular mass is the mass of a molecule expressed in atomic mass units. It is a dimensionless quantity.

The relative molecular mass of simple and complex substances equals the sum of the relative atomic masses of the atoms their molecule consists of. For example, the relative atomic mass of oxygen is 16, while the relative molecular mass of oxygen is 32 and of ozone is 48. The relative molecular mass of sulphuric acid H_2SO_4 is $1 \times 2 + 32 + 16 \times 4 = 98$.

The amount of a substance is a physical concept. It implies the number of structural units or entities (atoms, molecules, ions, or other particles) forming the substance. It is designated by the letter n (or the Greek letter ν).

In practice, one has to do not with individual atoms and molecules, but with much larger amounts of substances.

The unit of the amount of substance is the mole. It is the amount of substance of a system that contains as many elementary entities as there are carbon atoms in 0.012 kilogramme of $^{12}_{6}C$, i.e. 6.02×10^{23} entities. For example, the mass of 6.02×10^{23} molecules of sulphuric acid is 98 g (the number of molecules multiplied by the relative molecular mass of one molecule in atomic mass units and by the value of the amu in grammes, i.e. $6.02 \times \times 10^{23} \times 98 \times 1.66 \times 10^{-24}$).

The mass of one mole of a substance is called its molar mass M.

This quantity is obtained by dividing the mass of a substance in grammes by the amount of the substance in moles and is therefore expressed in g/mol. It coincides numerically with the relative molecular mass of a substance (or the relative atomic mass of an element). For instance, the molar mass of Cl_2 is 71 g/mol, of NaCl is 58.5 g/mol, of Na is 23 g/mol, and of Ca is 40 g/mol. The number of entities in one mole of a substance, i.e. 6.02×10^{23}, is called the **Avogadro number** or **constant** (N_A).

The number of moles, the molar mass, and the mass of a substance are related to one another by the formula $M = m/n$. Hence, any of these quantities can be determined if the other two are known. For example, the number of moles in 196 g of H_2SO_4 ($m = 196$ g) whose molar mass is $M = 98$ g/mol is $n = m/M = 196/98 = 2$ mol.

Atoms combine into molecules in accordance with their valence, therefore, on the one hand, proceeding from the formula of a substance, we can determine the valence of the atoms of the elements it contains. On the other hand, the formula of a chemical compound is generally compiled proceeding from the valence of the relevant elements.

The valence of an atom of an element is its ability to form chemical bonds.

The valence is determined by the number of bonds formed by atoms of a given species with other ones. A hydrogen atom can form only one bond with other atoms, therefore its valence has been adopted as unity. Consequently, the valence of nitrogen in ammonia NH_3 is three, and of sulphur in H_2S is two.

Since compounds with hydrogen have not been obtained for all the elements, it was found more expedient to use oxygen compounds for determining the valence. Knowing the composition of an oxygen compound of a given element, one can determine its valence by having in view that an oxygen atom always attaches two atoms of a monovalent element. For example, the valences of sodium, calcium, and silicon in the compounds Na_2O, CaO, and SiO_2 are one, two, and four, respectively.

The valence of the atoms in each specific substance is constant.

Therefore, *any pure substance has a constant composition regardless of how it was obtained.* This statement is known as **the law of definite proportions** or **constant composition.**

The development of the theories of the structure of an atom and of a chemical bond was attended by further development of the notions of valence.

In addition to the ways of determining the valence according to compounds with hydrogen and oxygen considered above, the valence of atoms in more complex molecules is found from the number of chemical bonds formed by a given atom. For instance, in acetylene C_2H_2, each of the carbon atoms forms four bonds (its structural formula is H—C≡C—H).

Consequently, proceeding from the formula of a substance, we can determine: (a) the valences of the atoms of the elements forming a molecule of the substance; (b) the atomic ratio; (c) the ratio of the atomic masses; and (d) the percentage by mass of each element in the substance.

Example 1. Knowing the formula of a substance, e.g. SO_3, determine the mass fraction (%) of each element.

We determine the valence, knowing that for a substance consisting of two elements the product of the valence of one element and the number of its atoms in a molecule equals this product for the other element.

The valence of oxygen is two, hence for the oxygen in the molecule we have $2 \times 3 = 6$. The valence of the single sulphur atom in the molecule is 6:1 = 6.

The atomic ratio in a molecule of SO_3 is 1:3, i.e. it contains one atom of sulphur and three atoms of oxygen.

Knowing the atomic masses of the elements, i.e. $A_r(S) = 32$ and $A_r(O) = 16$, we compute their ratio in SO_3: $32:(3 \times 16) = 2:3$.

The relative molecular mass of SO_3 is $M_r = 32 + 3 \times 16 = 80$.

Consequently, the mass fraction x of sulphur in sulphur trioxide in per cent can be found

by the formula

$$x(\mathrm{S}) = \frac{A_r(\mathrm{S})}{M_r(\mathrm{SO_3})}\,100\%; \quad x(\mathrm{S}) = \frac{32}{80} \times 100 = 40\%$$

Since the remainder is oxygen, we have $x(\mathrm{O}) = 100 - 40 = 60\%$

Example 2. Proceeding from the valences of the elements boron and oxygen, find the formula of a compound of these two elements.

Boron is trivalent and oxygen is divalent. The atoms in a chemical compound cannot have free valences. Consequently, the sum of the valences of all the boron atoms in the compound must equal that of all the oxygen atoms. The least common multiple of three and two is six, hence, the total number of valences of both boron and oxygen in the compound is six. Since each boron atom is trivalent, a molecule must contain two boron atoms. Similarly, the number of oxygen atoms in a molecule is 6:2 = 3. Therefore, the compound has the formula B_2O_3.

Questions and Problems

1. Why are the atomic and molecular masses called relative? Why are these quantities dimensionless? Write their symbols.
2. What quantitative data can be obtained on the basis of a chemical formula?
3. What is the transient quantity M (the molar mass) needed for?
4. A substance is known. How can one pass over from its amount to its mass?
5. What does "$M(H_3PO_4)$ = 98 g/mol" signify?
6. "The molar mass is the mass of a mole of a substance". Is this statement correct? Why?
7. A substance has the formula C_2H_6O. Give a complete as possible quantitative characteristic of it and perform the required calculations.
8. Substances have a constant composition. Explain why.
9. The valences of Na, Al, Ca, N, Ag, Mg, Zn, K, and Si are 1, 3, 2, 5, 1, 2, 2, 1, and 4, respectively. Write the formulas of their oxides.
10. The formula of sulphuric acid is H_2SO_4, and of potassium chlorate is $KClO_3$. Determine the percentage by mass of each element in these compounds.

1.4. Avogadro's Law and the Molar Volume of Gases

Any specimen of a substance is characterized not only by quantitative indices such as the mass and the amount of substance, but also by the volume. Measurements of the volume are especially important for gases.

J. Gay-Lussac, when studying the reaction of gaseous substances, arrived at the **law of combining volumes**: when gases react, the volumes consumed and produced, measured at the same temperature and pressure, are in ratios of small integers. For instance, for the reaction

$$\mathrm{N_2(g) + 3H_2(g) = 2NH_3(g)}$$

the volumes of the reacting and produced gases are in the ratio of 1:3:2.

To explain this law, A. Avogadro advanced a hypothesis, which was confirmed experimentally and named Avogadro's law:

equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules.

Two important corollaries follow from Avogadro's law. The first of them is as follows:

The same number of molecules of different gases at the same temperature and pressure will occupy the same volume.

One mole of a gas, which contains 6.02×10^{23} molecules, will occupy a volume of 22.4 litres at standard temperature and pressure (STP), i.e. at 273 K (0° C) and 101 325 Pa. If n moles of a gas occupy a volume of V, we can find the molar volume of the gas by the formula $V_m = V/n$. This formula can be used to determine the volume of a gas if we know its amount and, conversely, to find the amount of a gas occupying a given volume.

Knowing the density of a gas ϱ, we can calculate its mass: $m = V\varrho$. Since $V = V_m n$ and $m = Mn$, we find by substitution into the formula $m = V\varrho$ that $Mn = V_m n\varrho$. Cancelling n, we obtain $M = V_m\varrho$, whence $\varrho = M/V_m$. Since for standard temperature and pressure $V_m = 22.4$ lit/mol, we have $\varrho = M/22.4$.

This relation is very important for understanding the second corollary that is associated with the relative density of gases d.

The relative density of a gas is a quantity showing how many times the gas is heavier (lighter) than another one, i.e. how many times the density of the gas is larger (smaller) than that of the other one.

The relative density equals the ratio of the densities of the gases, namely, $d = \varrho_1/\varrho_2$. Inserting into this formula the expressions for the densities, we obtain:

$$d = \frac{M_1/22.4}{M_2/22.4} = \frac{M_1}{M_2}$$

In other words, *the relative density of a gas is the ratio of the molar mass of the gas being studied to that of a reference gas.* The relative density is a dimensionless quantity.

Since the molar mass of a substance is numerically equal to its relative molecular mass, i.e. $M = M_r$, the formula for the relative density can be written as $d = M_r'/M_r''$. Hence, to calculate the relative density, it is sufficient to know the relative molecular masses of gases.

The reference gas used is indicated by the relevant subscript. For instance, d_{H_2} signifies that hydrogen is the reference gas, and we call it the "density relative to hydrogen"; d_a is the density relative to air; d_{O_2} is the density relative to oxygen. The chemical formula of the gas being studied is placed in parentheses after the density symbol: $d_{H_2}(Cl_2)$ is the density of chlorine relative to hydrogen.

Knowing the relative density, we can compute the relative molecular mass and also molar mass of a gas whose formula is unknown:

$$M_r(X) = d_{H_2} M_r(H_2)$$
$$M(X) = d_{H_2} M(H_2)$$

where $M_r(H_2) = 2$; if air is used as the reference gas, its average relative molecular mass is taken equal to 29.

The molar mass of a gas can be determined proceeding from its molar volume at STP using the formulas $n = m/M$ and $n = V/V_m$. For the same number of moles of the same gas, we have $m/M = V/V_m$. Consequently, $M = mV_m/V$. At STP, $V_m = 22.4$ lit/mol. Therefore, $M = 22.4\ m/V$. It also follows from this formula that $V = 22.4\ m/M$.

Under conditions differing from standard temperature and pressure, the volume of a gas is reduced to the standard ones (STP) by using an equation including **Boyle's and Gay-Lussac's gas laws:**

$$\frac{pV}{T} = \frac{p_0 V_0}{T_0}$$

where V is the volume of a gas at the pressure p and temperature T, and V_0 is the volume of the gas at STP (the pressure p_0 and temperature T_0).

The Clapeyron-Mendeleev equation is also used to find the molar masses:

$$pV = \frac{m}{M} RT$$

where m is the mass of a gas, g, and R is the molar gas constant equal to 8.314 J/(mol·K).

If the volume of a gas is expressed in litres, the above equation becomes

$$pV = 1000 \frac{m}{M} RT$$

It is customary practice to convert the volumes of gases to STP, i.e. a temperature of 273 K and a pressure of 101.325 kPa.

The above ways of evaluating the molar masses can be applied not only to gaseous substances, but also to all substances that can pass into the gaseous state without decomposition when heated.

Example 1. Calculate the volume of the following gases at STP if there have been taken: (a) 2 mol of nitrogen; (b) 56 g of nitrogen; (c) 16 g of oxygen; and (d) 0.5 mol of oxygen.

Solution.

(a) $V = V_m n$. Since $n = 2$ mol, $V_m = 22.4$ lit/mol, then $V(N_2) = 22.4$ lit/mol × × 2 mol = 44.8 lit.

(b) $V(N_2) = 22.4\ m/M$. Since $m = 56$ g and $M = 28$ g/mol, we have $V(N_2) =$ $= 22.4 \times 56/28 = 44.8$ lit.

(c) $V(O_2) = 22.4\ m/M$. Since $m = 16$ g and $M = 32$ g/mol, we obtain $V(O_2) =$ $= 22.4 \times 16/32 = 11.2$ lit.

(d) $V(O_2) = V_m n$. Since $V_m = 22.4$ lit/mol and $n = 0.5$ mol, then $V(O_2) = 22.4 \times$ × 0.5 = 11.2 lit.

Example 2. We have 1 lit of H_2, 3 lit of NH_3, and 2 lit of O_2 under the same conditions. What number of molecules is contained in each volume?

Solution. By Avogadro's law, equal volumes of different gases under the same conditions contain the same number of molecules.

Let us find the number of molecules in 1 lit of H_2:

22.4 lit of H_2 contain 6.02×10^{23} molecules

1 lit of H_2 contains x molecules

Hence, $x = 6.02 \times 10^{23}$: $22.4 = 2.69 \times 10^{22}$ molecules.

The gases are under identical conditions, therefore by Avogadro's law, the number of molecules in 3 lit of NH_3 is three times larger than in 1 lit of H_2 ($3 \times 2.69 \times 10^{22} = 8.07 \times 10^{22}$ molecules), while in 2 lit of O_2 it is twice the number in 1 lit of H_2 ($2 \times 2.69 \times 10^{22} = 5.38 \times 10^{22}$ molecules).

Example 3. A mixture of ozone and oxygen has a density relative to hydrogen of 18. Determine the composition of the mixture in per cent by volume.

Solution. We determine the molar mass of the mixture:

$$M = 2d_{H_2} = 2 \times 18 = 36 \text{ g/mol}; \quad m = 36 \times 1 = 36 \text{ g}$$

Consequently, 36 g of the mixture occupy a volume of 22.4 lit.

Let the mass of the oxygen in the mixture be m_1. Therefore, the mass of the ozone will be $(36 - m_1)$ g; let the volume of the oxygen in the mixture be V_1, hence the volume of the ozone will be $(22.4 - V_1)$ lit.

Proceeding from Avogadro's law, we compile a proportion:

(a) 32 g of O_2 occupy a volume of 22.4 lit
m_1 g of O_2 occupy a volume of V_1 lit
$$\frac{32}{m_1} = \frac{22.4}{V_1}$$

(b) 48 g of O_3 occupy a volume of 22.4 lit
$(36 - m_1)$ g of O_3 occupy a volume of $(22.4 - V_1)$ lit
$$\frac{48}{36 - m_1} = \frac{22.4}{22.4 - V_1}$$

From proportion (a), we find V_1 and insert it into proportion (b):

$$V_1 = \frac{22.4 m_1}{32} = 0.7\ m_1$$

$48(22.4 - V_1) = 22.4(36 - m_1)$;

$48(22.4 - 0.7\ m_1) = 22.4(36 - m_1)$, whence $m_1 = 24$ g.

The mass of the oxygen in the mixture is 24 g.

The volume of O_3 in the mixture is $22.4 - V_1$. From proportion (a) we have found that $V_1 = 0.7\ m_1$, hence $V_1 = 0.7 \times 24 = 16.8$ lit. Consequently, the volume of O_3 in the mixture is $22.4 - 16.8 = 5.6$ lit.

We find the composition of the mixture in per cent by volume. The total volume of the mixture is 22.4 lit, or 100%, whence the content of O_2 in the mixture is $(16.8/22.4) \times 100\% = 75\%$ (by volume), and the content of O_3 is $100 - 75 = 25\%$ (by volume).

Questions and Problems

1. All gases obey Avogadro's law, whereas liquids and solids do not obey it. Explain why.
2. The value of the molar volume is the same for any gases under the same conditions. How can you explain this?
3. What does the notation $d_{H_2}(CO_2) = 22$ mean?
4. What is the relation between the concepts "molar mass" and "molar volume"?
5. How can one find the volume of a gas if its amount is known?

1.5. Chemical Equations. The Law of Conservation of Mass. Calculations on the Basis of Chemical Equations

Substances can experience various transformations. For example, water when boiling transforms into the gaseous state (vapour), and when cooled it becomes crystalline (ice). Water can be decomposed into its elements—hydrogen and oxygen. The heating or cooling of water changes only its state of aggregation, but does not break the chemical bond between the hydrogen and oxygen. The decomposition of water yields two gaseous substances—hydrogen and oxygen—that differ from water in their physical and chemical properties. Consequently, one phenomenon does not change the qualitative and quantitative composition of substances, whereas another one changes both of them. Accordingly, physical and chemical phenomena are distinguished.

Phenomena in which the state of aggregation of a substance and its shape change, but its qualitative and quantitative composition and, therefore, chemical properties, do not change are called physical.

Phenomena in which substances experience changes in their qualitative and quantitative composition producing new substances that differ from the initial ones are called chemical.

Chemical reactions are processes of the conversion of substances into other ones. A chemical reaction can be represented symbolically by a **chemical equation.** Every formula in an equation must strictly correspond to the composition of the substances participating in the reaction.

The amounts of substances corresponding to the equation of a reaction are called the **stoichiometric amounts.** Stoichiometric calculations are based on two very important principles, namely, (1) the composition of any substance is expressed by a definite formula, and (2) the substances react in strict accordance with the law of conservation of mass:

in any chemical process, the mass of the substances entering into a reaction equals the total mass of the substances obtained after the reaction.

As shown by A. Einstein, however, this law has limitations. In chemical reactions, no measurable changes in mass occur because atoms do not vanish and are not created again, but only regroup from one combination into another one. The relation between mass and energy is known from the course in physics. The mass of a substance that has transformed into an equivalent amount of radiation and vice versa can be calculated from Einstein's equation $E = mc^2$, where E is the energy, m is the mass, and c is the speed of light in vacuum.

Chemical reactions are known to be attended by the evolution or absorption of energy, hence the mass of the reactants should also change. For example, in the thermal dissociation of a hydrogen molecule, about

436 kJ is absorbed, which corresponds to a change of 2.5×10^{-9} g in the mass. This value is below the sensitivity limit of an analytical balance, therefore it is considered that the law of conservation of mass is observed strictly.

Consequently, the relation between mass and energy reflects a most important law of nature—the law of conservation of matter (of infinity of matter).

Like other laws of nature, the **law of conservation of mass** is of a major practical significance because it enables one to establish the quantitative relations between substances experiencing chemical transformations.

The correctness of this law is explained by the presence of the same number of like atoms before and after a reaction (matter cannot vanish). When writing a chemical equation, this condition is observed by choosing the appropriate coefficients, i.e. by balancing the equation.

For example, when sodium sulphate is reacted with barium chloride, an exchange reaction proceeds yielding sodium chloride and barium sulphate:

$$Na_2SO_4 + BaCl_2 \rightarrow NaCl + BaSO_4 \downarrow$$

Although the formulas of the reactants and products have been written correctly, this notation of the course of the reaction is not yet a reaction equation because the law of conservation of mass has meanwhile not yet been observed. To obey this law, it is necessary to balance the number of atoms on each side of the equation by choosing the relevant coefficients. After doing this, the equation of the above reaction becomes:

$$Na_2SO_4 + BaCl_2 = 2NaCl + BaSO_4 \downarrow$$

When writing the equations of reactions, the physical state of each component is often indicated by writing to the right of its formula the relevant symbol in parentheses: g—gaseous, lq—liquid, s—solid, and aq—an aqueous solution. For instance:

$$2Na(s) + 2H_2O(lq) = 2NaOH(aq) + H_2(g)$$

A chemical reaction rarely proceeds in accordance with the quantitative relations shown in the equation, however. In this case, calculations must be performed.

Example 1. What mass of magnesium oxide forms in the combustion of (a) 0.5 mol of magnesium, and (b) 4 g of magnesium.

(a) *Given*:

$n(Mg) = 0.5$ mol

$m(MgO) = ?$

Solution. We write the chemical equation and balance it:

$$\underset{2\text{ mol}}{2Mg} + O_2 = \underset{2\text{ mol}}{2MgO}$$

The equation shows that two moles of magnesium enter into the reaction and two moles of magnesium oxide form, i.e. the molar ratio is 1:1.

By the conditions of the example, 0.5 mol of magnesium burns. Consequently, 0.5 mol of magnesium oxide forms. We calculate the mass by the formula $m = Mn$. Since $M(MgO) = 40$ g/mol, we have:

$$m(MgO) = 40 \text{ g/mol} \times 0.5 \text{ mol} = 20 \text{ g}$$

(b) *Given*:

$m(Mg) = 4$ g

$m(MgO) = ?$

Solution

$$\underset{2 \text{ mol}}{2Mg} + O_2 = \underset{2 \text{ mol}}{2MgO}$$

The molar ratio is 1:1;
$m = Mn$; hence $m(Mg) = 24 \times 1 = 24$ g and $M(Mg) = 24$ g/mol;
$m(MgO) = 40 \times 1 = 40$ g, and $M(MgO) = 40$ g/mol.
The mass ratio of Mg and MgO is 24:40 = 3:5
We compile a proportion:

3 g of Mg yield 5 g of MgO
4 g of Mg yield x g of MgO

$$x = \frac{5 \times 4}{3} \approx 6.7 \text{ g}$$

Having the data of elemental analysis, one can determine the formula of a specific compound.

Example 2. The combustion of 1.3 g of an unknown hydrocarbon yielded 4.4 g of CO_2 and 0.9 g of H_2O. The molar mass of the hydrocarbon is 78 g/mol. Determine its formula.

Given:

$m(CO_2) = 4.4$ g
$m(H_2O) = 0.9$ g
$M(C_xH_y) = 78$ g/mol

$x = ?$, $y = ?$

Solution. We write the scheme of the reaction:

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O$$

Since the products contained 4.4 g of CO_2, we can determine the mass of the carbon in the sample knowing that $M(CO_2) = 44$ g/mol and $M(H_2O) = 18$ g/mol.

12 g of C yield 44 g of CO_2
z g of C yield 4.4 g of CO_2

$$z = 1.2 \text{ g}$$

We calculate the mass of the hydrogen:

2 g of H_2 yield 18 g of H_2O
~~z g of H_2 yield 0.9 g of H_2O~~

$$z = 0.1 \text{ g}$$

Since the total mass of the hydrogen and carbon equals 1.3 g (i.e. 1.2 + 0.1), which is the initial mass of the sample, the substance consists of carbon and hydrogen. The masses of the carbon and hydrogen in the taken sample are in the ratio of 1.2:0.1. The atomic masses of carbon and hydrogen, on the other hand, are in the ratio 12:1. We find from the proportion $\frac{1.2}{12} : \frac{0.1}{1}$ that the atomic ratio is 1:1, therefore the empirical (simplest) formula is CH, i.e. $x = y$.

The molar mass of the substance being analysed (C_xH_x) is $M = 78$ g/mol. Hence, $x = 78:(12 + 1) = 6$, and the true formula of the substance is C_6H_6.

Calculations by equations can be carried out with account taken of the volume of gases.

Example 3. How many litres of carbon dioxide are evolved when hydrochloric acid reacts with 25 g of calcium carbonate?

Given:
$m(CaCO_3) = 25$ g
$V(CO_2) = ?$

Solution. We write the equation of the reaction:

$$\underset{1\text{ mol}}{CaCO_3} + 2HCl = CaCl_2 + H_2O + \underset{1\text{ mol}}{CO_2}\uparrow$$

The molar ratio of $CaCO_3$ and CO_2 is 1:1.

By the conditions of the example, the mass of the $CaCO_3$ is 25 g. Since $n = m/M$, then $n(CaCO_3) = 25$ g/100 g/mol = 0.25 mol.

The molar ratio of $CaCO_3$ and CO_2 is 1:1, therefore $n(CO_2) = 0.25$ mol.

We find the volume by the formula $V = V_m n$. Since the molar volume of CO_2 is $V_m = 22.4$ lit/mol, we obtain $V(CO_2) = 22.4 \times 0.25 = 5.6$ lit.

Example 4. What volume of oxygen is needed for the combustion of 3.36 lit of ethylene?

Since the molar volume of any gas is constant at STP and equals 22.4 lit/mol, calculations with gaseous substances are substantially simplified. The ratio between the volumes of gases becomes equal to their molar ratio.

Given:
$V(C_2H_4) = 3.36$ lit
$V(O_2) = ?$

Solution. We write the equation of the reaction:

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$

The molar ratio of ethylene and oxygen is 1:3. We can therefore write the proportion $1:3 = 3.36:V(O_2)$. Hence, $V(O_2) = 3.36 \times 3 = 10.08$ lit.

Example 5. A mixture of nitrogen and oxygen with a volume of 15 lit was mixed with hydrogen and exploded. After bringing the residual gases to standard temperature and pressure, the volume decreased by nine litres. Find the composition of the initial mixture in per cent by volume. (When solving the problem, have in view that all the oxygen entered into the reaction and no excess hydrogen remained.)

Given:
$V(N_2 + H_2) = 15$ lit
$\Delta V = 9$ lit
Vol. fraction (%) of $N_2 = ?$
Vol. fraction (%) of $H_2 = ?$

Solution. The volume of the reacted gases is 9 lit. By the conditions of the example, the oxygen and hydrogen react by the equation

$$2H_2 + O_2 = 2H_2O$$

The molar ratio of the gases is 2:1, consequently the volume ratio is also 2:1. There are altogether three volume parts.

Since the volume of the reacted mixture is 9 lit, and the oxygen forms one-third of this volume, the volume of the oxygen is 9:3 = 3 lit.

The volume fraction (%) of the oxygen in the initial mixture (15 lit) was $(3:15) \times 100 = 20\%$. The remainder is nitrogen, i.e. the volume fraction (%) of the nitrogen is $100 - 20 = 80\%$.

Example 6. After the explosion of 20 ml of a mixture of hydrogen and oxygen, 3.2 ml of the oxygen remained. Determine the volume of each of these gases in the initial mixture.

Given:
$V(H_2 + O_2) = 20$ ml
$\Delta V(O_2) = 3.2$ ml
$V(O_2) = ?$
$V(H_2) = ?$

Solution. Since 3.2 ml of unreacted oxygen remained after the explosion, the total volume of the reacted oxygen and hydrogen is

$$20 - 3.2 = 16.8 \text{ ml}$$

We write the equation of the reaction:

$$2H_2 + O_2 = 2H_2O$$

It follows from the reaction equation that the hydrogen and oxygen react in the volume ratio 2:1, i.e. the total volume of the reacting gases is 3 parts, and the oxygen is one-third of this amount.

Since the volume of the reacted mixture is 16.8 ml, the volume of oxygen in it is 16.8:3 = 5.6 ml. The volume of the hydrogen in it is 5.6 × 2 = 11.2 ml.

It is known from the initial conditions that after the explosion, the volume of the unreacted oxygen was 3.2 lit. Hence, the total volume of the oxygen prior to the reaction was 5.6 + 3.2 = 8.8 ml.

Consequently, the volume of the hydrogen in the mixture was 11.2 ml and of oxygen was 8.8 ml.

Questions and Problems

1. Everything in nature obeys the law of conservation of mass. How does a chemical reaction obey this law?

2. Explain the principle of selecting stoichiometric coefficients for balancing reaction equations.

3. Write down and give a complete qualitative and quantitative characteristic of the reaction equation $CO_2 + 2NaOH = Na_2CO_3 + H_2O$.

4. How many grammes of sodium hydroxide must be reacted with hydrogen chloride to obtain 234 g of sodium chloride?

5[a]. The burning of 1.2 g of a hydrocarbon yielded 3.3 g of CO_2 and 2.7 g of H_2O. Find the empirical formula of the hydrocarbon *.

6[a]. Given 50 g of C_6H_{12}. How many grammes of carbon and hydrogen are contained in this sample?

7[a]. A liquid contains 11.19% of hydrogen and 88.81% of oxygen. What are the relative amounts of hydrogen and oxygen atoms in the liquid?

8[a]. When roasting 49 g of a potassium salt containing chlorine and oxygen until the latter stopped evolving, the solid residue with a mass of 29.8 g was KCl. Determine the formula of the initial salt.

SUMMARY

An atom, element, and molecule are the most important concepts in chemistry. The diversity of chemical compounds is determined by the reaction of atoms with one another to form simple or complex substances. The atoms of a single element can form several simple substances, which is called allotropy. Every compound is characterized by its qualitative and quantitative composition, which is constant for the molecules of a substance. The composition of simple and complex substances can be depicted by the symbols of the atoms of the relevant chemical elements with an indication of their number.

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* The answers to problems with the superscript [a] on their numbers are given at the end of the book.

Atoms and molecules have a definite mass. Two ways of indicating it are used in chemistry, namely, the absolute atomic (molecular) mass and the relative atomic (molecular) mass. The latter is sometimes called the atomic (molecular) weight. The phenomena proceeding with the participation of simple and complex substances can be divided into physical and chemical ones.

CHAPTER 2

THE PERIODIC LAW AND PERIODIC TABLE OF ELEMENTS IN THE LIGHT OF THE THEORY OF STRUCTURE OF AN ATOM

OBJECTIVES

To characterize the most important constituent parts of an atom—a nucleus, electron, proton, and neutron; to explain the concept of an atomic orbital proceeding from the corpuscular and wave duality of an electron; to describe the shapes of the *s* and *p* orbitals; to depict the electron configurations of atoms; to characterize the ionization energy (potential), electron affinity, electronegativity, and the radius of an atom; to explain the laws of the changes in the metallic and non-metallic properties of the elements in the periods and groups of the periodic table; to show the general laws of the changes in the properties of oxides and hydroxides in a period and in a group; to explain the periodic law from the standpoints of the present notions on the structure of an atom.

2.1. Discovery of the Periodic Law

The creation of the atomic and molecular theory and the discovery of new chemical elements promoted the development of the theory of an element. The attempts of scientists to uncover the relation between chemical elements from both a qualitative and quantitative viewpoints were quite lawful.

The first attempt to classify the elements was made by A. Lavoisier, and then by J. Berzelius. This is how the elements became divided into metals and non-metals.

This division was made only on the basis of qualitative characteristics, i.e. the properties of the elements. The search for the reason why the properties differ led scientists to the necessity of relating the qualitative and quantitative characteristics of elements. The atomic mass of an element was considered to be its basic quantitative characteristic. This is why the efforts of scientists were aimed at studying the relation between the properties of elements and their atomic masses. All this paved the way to the discovery of the periodic law. A major role was also played by the International chemical congress at Karslruhe (1860). By this time already 63 chemical elements were known.

Like his predecessors, D. Mendeleev chose the atomic mass as the main characteristic unambiguously determining a chemical element. But in contrast to them, Mendeleev sought laws in the change in the atomic masses not only in chemically similar elements within one natural group, but also for unsimilar elements. He arranged the elements in series (which he called periods) beginning with an alkali metal and ending with a noble gas in accordance with their increasing atomic masses. He wrote the following periods under the preceding ones to bring elements having similar properties into the same vertical column, or group.

March 1, 1869 is the date of discovery of the periodic table by Mendeleev. The table in use today supplemented with the elements discovered after Mendeleev's time is given at the beginning of the book. A long-period variant of it is given at the end of the book.

When studying the properties of the chemical elements, Mendeleev gave special attention to the atomic mass, the crystalline form, density, atomic volume, and the kinds of compounds.

The periodic table enabled Mendeleev to make the following conclusions: (1) when the elements are arranged in the order of their increasing atomic mass, their properties periodically repeat, i.e. the atomic mass determines the properties of an element; (2) the elements with low atomic masses are typical ones, their occurrence in nature is the greatest, and their properties are sharply pronounced; (3) the discovery of many more unknown (at his time) elements can be expected; and (4) correction of the atomic masses of the elements can be expected. These conclusions allowed him to formulate the periodic law: *the properties of simple bodies, as well as the forms and properties of the compounds of the elements, are periodic functions of the atomic masses (weights) of the elements.*

The discovery made by Mendeleev only triggered off the development of a natural system of chemical elements. The basic principle was established which states that the physical and chemical properties of simple substances and compounds are a periodic function of the atomic mass of the elements. This signified that a new law of nature was discovered.

On the basis of the periodic table, Mendeleev predicted the existence of eleven new, hitherto undiscovered elements. Already during Mendeleev's lifetime, new elements were discovered. This confirmed the correctness of the law and fortified its place in science.

In 1875, the French chemist Lecoq de Boisbaudran discovered gallium (eka-aluminium), in 1879, L. Nilson in Sweden discovered scandium (eka-boron), and in 1886, C. Winkler in Germany discovered germanium (eka-silicon).

The periodic law, which showed the relation between the properties of the elements and their atomic masses, was irrefutable. The subsequent discovery of new, precised atomic masses of already discovered elements convinced scientists in its correctness. But the reasons explaining this periodicity remained unknown up to the appearance and development of the theory of the structure of an atom.

Questions and Problems

1. The atomic mass of the elements was chosen by scientists as the leading feature for their classification. Why?
2. What is the difference between Mendeleev's classification of the elements and those of his predecessors?
3. What important conclusions did Mendeleev make from his periodic table?

2.2 Structure of the Atom. Atomic Nuclei

Up to the 1870's, the indivisibility of an atom was taken to be an axiom, therefore it was difficult to understand and explain cathode radiation when it was discovered by W. Crookes (1832-1919). It was shown experimentally that cathode rays are a stream of negatively charged particles.

In 1895, W. Roentgen (1845-1923) discovered a new kind of radiation called X rays.

In 1896, the French physicist A. Becquerel (1852-1908) studied several fluorescing substances that could be sources of penetrating radiation similar to X rays. Among the multitude of substances he studied, only uranium compounds acted on a photographic plate protected by black paper. Becquerel found that all uranium compounds emit rays identical to X rays in their properties. In the same year, Pierre Curie together with his wife, Marie Sklodowska-Curie, inaugerated a detailed investigation of the phenomenon discovered by Becquerel. While studying uranium ore, in 1898, they reported on the discovery of a new element—polonium. Somewhat later, they discovered another element—radium—whose spontaneous emission was much higher than that of uranium. The property of substances to spontaneously emit radiation is called **radioactivity.**

E. Rutherford (1871-1937) showed that a magnetic field causes radioac-

tive radiation to differentiate into alpha, beta, and gamma radiation. That radioactive radiation is associated with a complicated process—the disintegration of atoms—is an incontrovertible fact. This indicates that an atom is indivisible only chemically, whereas physically it is divisible and has a discrete structure. This conclusion was supported still more by the further studying of cathode rays, which resulted in the discovery of the electron, a constituent part of an atom.

An **electron** is the lightest elementary particle in an atom. It carries a negative electric charge equal to 1.602×10^{-19} C. The charge of an electron is conditionally adopted to be -1. The mass of an electron is 9.1095×10^{-28} g, which is 1/1836 of the mass of the lightest element—hydrogen. An electron is designated by the symbol e^-.

The outstanding achievements in the field of the natural sciences (the discovery of radioactivity, the electron, etc.) nullified the old metaphysical notions of the indivisibility of an atom and of the unchangeability of the chemical elements.

In 1924, Louis de Broglie advanced the hypothesis that all objects of the microworld are characterized by a dual nature and simultaneously have properties of a particle and a wave. The wave nature of an electron was proved experimentally: a beam of electrons scattered by a crystal produces the same diffraction pattern as X rays do.

In 1926, E. Schrödinger (1887-1961), proceeding from the notion of electrons having wave properties, showed that the motion of an electron can be described by a wave function. An electron in an atom should be considered as a blurred distribution of a negative charge in the form of an "electron cloud". According to quantum mechanics, the probability of an electron being far from the nucleus of an atom is very small, although this may happen. We can therefore speak of a definite region beyond whose limits this probability can be disregarded.

The region in space in which the probability of finding an electron is maximal is called an orbital.

An orbital is the complete set of wave functions of an electron in an atom. Consequently, for each given wave function, there is a boundary surface within which a definite fraction of an electron's charge is concentrated. The maximal electron density corresponds to the greatest probability of finding an electron at the relevant place. Hence, the concept of an orbital implies the shape of an **electron cloud** that changes depending on the density of the negative charge. Orbitals can differ from one another in the energy needed for removing a negative charge, in the shape of the electron cloud, and in the orientation of the electron cloud relative to the centre of symmetry—the atomic nucleus. These features reveal the discreteness of the characteristics of an electron and the quantized nature of its properties.

The characteristics of orbitals, namely, their energy, shape, and orientation in space, can be set by definite numbers known as **quantum numbers.**

The electrical neutrality of free (unbonded) atoms indicates that they should contain the same number of positive and negative units of electricity.

When a hydrogen atom loses an electron, a particle forms that carries a single positive charge. It is called a **proton.** The charge of a proton is equal in magnitude and opposite in sign to the charge of an electron, while its mass is 1.67×10^{-24} g, which is 1836.12 times larger than the mass of an electron. A proton is designated by the symbol *p*.

Rutherford when studying the scattering of alpha particles (helium nuclei) through metal foil found that most of them continue their rectilinear motion. Some of these particles, however, changed their direction because they were completely reflected from the surface of the foil. These data led to the important conclusion that there is a very dense particle carrying a positive charge at the centre of an atom. This particle is called the **nucleus of an atom.** Here the main mass of an atom is concentrated.

In 1933, an electrically neutral particle called a **neutron** was discovered. Its mass is almost equal to that of a proton. A neutron is designated by the symbol *n*. Protons and neutrons are elementary particles contained in an atomic nucleus.

All the elements in the periodic table are numbered in consecutive order. These numbers are known as the **atomic numbers** of the relevant elements.

The nucleus of an atom is characterized first of all by two parameters—the charge *Z* (numerically equal to the atomic number) and the **mass number** *A*. The mass number is the sum of the number of protons and neutrons in a nucleus, and the atomic number indicates the number of protons in a nucleus. At present, the following notation is used to characterize atomic nuclei: the atomic number of the nucleus is written at the lower left of the symbol for the element, and the mass number at the upper left. For example, the nucleus of a carbon atom is designated as $^{12}_{6}C$. This means that the charge of the nucleus (and, consequently, the number of protons) is 6, and the mass number is 12. The number of neutrons can be found as the difference of the mass number and charge of the nucleus, i.e. $12 - 6 = 6$. Since the masses of a proton and neutron differ very little from each other, the mass number approximately indicates the relative mass of a nucleus. The mass numbers are always integers.

In 1913, H. Moseley established that *the charge of a nucleus of an element* (i.e. the number of protons in the nucleus of its atom) *coincides with the atomic number of the element in the periodic table.* For atoms to be electrically neutral, as is observed for a substance as a whole, every nucleus should be supplemented by a negative charge such that would balance its positive charge.

The atomic masses, like the mass numbers, should have integral values. In 1910, F. Soddy (1877-1956) found that in natural radioactivity, atoms of the same element can form that have identical charges of their nuclei, but different atomic masses. This is why in the course of the gradual refining of Mendeleev's periodic table, it became necessary to place several species of atoms of the same element having different masses into the same cells. Such twin atoms having the same charge of the nucleus, but different atomic masses, are called **isotopes**. Hence it is clear that when speaking of the atomic mass, we have in view the average value of all the atomic masses of the isotopes of a given element. Consequently, the tabulated values of the atomic masses are not integers. It follows that the nuclei of isotopes of the same element have the same number of protons (the charge of the nucleus), but a different number of neutrons. Hence:

a chemical element is a species of atoms having an identical charge of their nuclei.

The periodic table contains four pairs of elements that occupy positions not corresponding to their atomic masses. These are argon and potassium (with atomic numbers of 18 and 19 and atomic masses of 39.9 and 39.1, respectively), cobalt and nickel (with atomic numbers of 27 and 28 and atomic masses of 58.9 and 58.7), tellurium and iodine (with atomic numbers of 52 and 53 and atomic masses of 127.60 and 126.90), and thorium and protactinium (with atomic numbers of 90 and 91 and atomic masses of 232.03 and 231). After establishing the values of the atomic numbers and the structure of the nucleus, this violation of the general law was explained. It is associated with the presence in the preceding element of a higher content of heavy isotopes, and in the following one, conversely, light isotopes. The charge of the nuclei (the number of protons) that determines the atomic number of an element, however, changes strictly regularly.

Questions and Problems

1. Explain the physical meaning of the atomic number of chemical elements in the periodic table.
2. Using Mendeleev's periodic table of elements, calculate the number of neutrons in a nucleus of an atom of zirconium (No. 40), copper (No. 29), technetium (No. 43), chromium (No. 24), and iron (No. 26).
3. How many protons and neutrons are contained in the nuclei of the isotopes ^{35}Cl, ^{36}Cl, ^{37}Cl, ^{38}Cl, ^{39}K, ^{40}K, and ^{40}Ar?
4. Why is an atom of an element electrically neutral?
5. What explains the existence of isotopes?
6. Do the isotopes of the same element differ in the number of electrons in an atom? Why?
7. Why is it impossible to apply the laws of classical mechanics to microparticles?
8. What does the dual nature of an electron consist in?
9. Why is an electron in an atomic orbital considered as an electron cloud?

2.3. Quantum Numbers and Atomic Orbitals

The **principal quantum number** n is associated with the average distance to an electron from the nucleus, i.e. it characterizes the size of the electron cloud and determines the energy level of an electron in an atom. Electrons with the same value of the principal quantum number are in the same energy level. The principal quantum number can have only integral values: 1, 2, 3, 4, etc. The term electron layer is sometimes used instead of energy level. The energy levels characterized by values of $n = 1, 2, 3, 4$, etc. are sometimes designated as the K, L, M, etc. levels. A layer with $n = 1$ corresponds to the lowest or ground level of energy.

The **orbital** (second) **quantum number** l determines the shape of an orbital (electron cloud). The permissible values of l are limited by the value of the principal quantum number n; the orbital quantum number l can have integral values from 0 to $n - 1$, i.e. $l = 0, 1, 2, 3, \ldots, (n - 1)$. For instance, if $n = 3$, then l can have only the values 0, 1, and 2. The different values of the orbital quantum number $l = 0$, 1, 2, and 3 correspond to different orbital shapes, which are designated as s, p, d, and f orbitals.

Table 1 shows the relations between the values of n and l, from which it can be seen that there is only one s orbital for each value of n. When $n = 2$, there are also three p orbitals, when $n = 3$, there are also five d orbitals, and when $n = 4$, there are also seven f orbitals.

Consequently, each energy level has a set of orbitals with the same value of the principal quantum number.

Table 1

Permissible Values of the Quantum Numbers n and l

n	l	Designation of orbitals	Number of orbitals
1	0	1*s*	1
2	0	2*s*	1
	1	2*p*	3
3	0	3*s*	1
	1	3*p*	3
	2	3*d*	5
4	0	4*s*	1
	1	4*p*	3
	2	4*d*	5
	3	4*f*	7

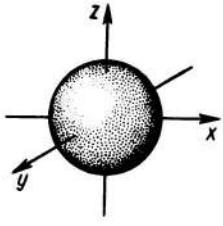


Fig. 1
Boundary surface of a 1*s* orbital

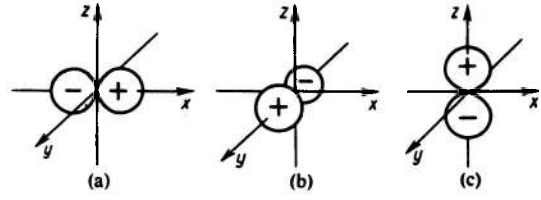


Fig. 2
p Orbitals of an atom:
a—$2p_x$ orbital; *b*—$2p_y$ orbital; *c*—$2p_z$ orbital

Orbitals of an identical shape in one energy level form a sublevel. Hence, we distinguish *s*, *p*, *d*, and *f* sublevels. It is obvious that not every energy level has the complete set of sublevels.

At $n = 1$, the orbital corresponding to the ground energy level is said to be a 1*s* orbital. Any *s* orbital has a spherical shape (Fig. 1). If $n = 2$, the *s* orbital of this level is designated as a 2*s* orbital, etc.

The 2*s* orbital in the second level is followed by three orbitals (p_x, p_y, p_z) with an equal energy called 2*p* orbitals. Each 2*p* orbital has the shape of a dumbbell arranged along the axis at right angles to the axes of the other two 2*p* orbitals (Fig. 2).

The third energy level from the nucleus ($n = 3$) should contain three sublevels: 3*s*, 3*p*, and 3*d*. The *d* sublevel consists of five orbitals (Fig. 3).

The fourth energy level ($n = 4$) already has four sublevels: 4*s*, 4*p*, 4*d*, and 4*f*. The *f* sublevel consists of seven orbitals.

Each orbital is depicted in the form of a contour accommodating the main part of the electron cloud.

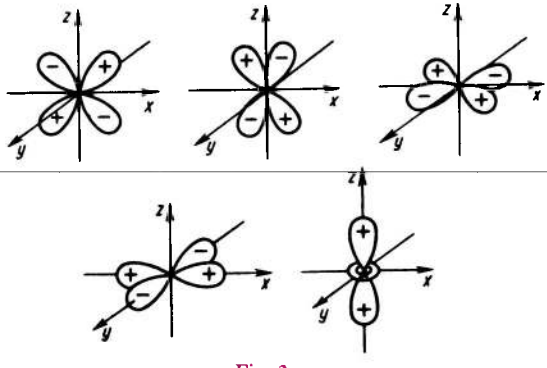


Fig. 3
3*d* Orbitals of an atom

In addition to the shape of an orbital, as we have already mentioned, the orientation of an orbital in space is also important. It is determined by the **magnetic quantum number** m_l. It is related to the orbital quantum number l and varies from $+l$ to $-l$, including zero. Consequently, the magnetic quantum number is a vector, i.e. not only a definite numerical value, but also a direction shown by the plus and minus signs corresponds to it.

The values of m_l characterize the "allowed" orientations of an electron cloud in space, while the number of allowed orientations is directly related to the shape of the electron cloud determined by the value of the orbital quantum number l. When $l = 0$, there can be only a single orientation of the electron cloud because it has the shape of a sphere. When $l = 1$, three allowed orientations of the cloud are possible: $m_l = -1$, 0, and $+1$. When $l = 2$, the number m_l has five allowed orientations: -2, -1, 0, $+1$, and $+2$.

The **spin quantum number** m_s characterizes the spin of an electron. Each electron can spin in one of two opposite directions, therefore m_s has two possible values: $+1/2$ and $-1/2$. Spins are also designated by oppositely directed vertical arrows: ↑ and ↓.

Questions and Problems

1. How do *s* and *p* orbitals differ from each other?
2. Which of the listed designations of atomic orbitals are never encountered: 1*p*, 1*s*, 2*p*, 2*d*, 3*f*, 4*f*, 4*p*?
3. Why is a *d* orbital less profitable from the energy viewpoint than a *p* orbital in the same energy level?
4. Why is it insufficient to know only the value of the principal quantum number to characterize the state of an electron in an atom?
5. Why is the number of electrons in an energy level limited?

2.4. Structure of the Electron Shells of Atoms

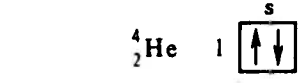
When describing the electron structure of many-electron atoms, we use the notions of orbitals in accordance with the concepts and characteristics mentioned above. It is very important here to know the laws of occupation by electrons of the energy levels of atoms (the **filling sequence** or **aufbau order**). It must always be had in view that if an atom is in its ground (unexcited) state, the electrons occupy the orbitals with the lowest energy. This is called the **principle of the least energy.**

Proceeding from the notions of the spin quantum number, W. Pauli (1900-1958) was the first to formulate the following law, now known as the **Pauli exclusion principle:**

no two electrons in any given atom can have exactly the same set of the four quantum numbers *n*, *l*, m_l, and m_s.

If one electron has, for instance, values of the quantum numbers $n = 1$, $l = 0$, $m_l = 0$, and $m_s = +1/2$, then a second electron in the atom can have the values $n = 1$, $l = 0$, $m_l = 0$, and $m_s = -1/2$. Consequently, there cannot be more than two electrons in any atomic orbital with given values of n, l, and m_l, and they must have opposite values of the spin quantum number. This signifies that the maximum capacity of any orbital is 2. When an orbital is occupied by two electrons with spins of $+1/2$ and $-1/2$, these electrons are said to be **paired.**

Proceeding from the Pauli exclusion principle, it is easy to calculate the maximum occupancy of the levels and sublevels in an atom. An *s* orbital can contain at most two electrons; the three *p* orbitals (p_x, p_y, and p_z) can accommodate altogether six electrons (two per *p* orbital); the five *d* orbitals can accommodate up to 10 electrons, the seven *f* orbitals—up to 14 electrons. Orbitals are customarily depicted by a box with the number of the sublevel written at its left and the symbol of the sublevel written on top. For example,



This can also be written as $1s^2$ (this is read "one *s* two"). Here the coefficient of the sublevel symbol indicates its belonging to the given level, while the exponent of the symbol indicates the number of electrons in the given sublevel.

The maximum number of electrons in a given level is determined by the formula

$$N_n = 2n^2$$

Let us depict for an example all the possible orbitals of an atom up to the fourth level (Fig. 4). The figure reveals how many sublevels there are in each level and how many orbitals there can be in each sublevel. This diagram also enables us to compare the store of energy in various sublevels, which is especially important when considering the sequence of occupation of the energy levels and sublevels by electrons. This sequence (the aufbau order) determines the electron configuration of an atom. The number of energy levels in an atom is determined by the number of the period in the periodic table in which the given element is.

When filling the energy levels, electrons tend to occupy different orbitals because this reduces the forces of their mutual repulsion as particles of a like charge. Being in separate orbitals, electrons have parallel spins (i.e. the same direction of their spins). These features indicate that *the configuration containing the largest number of unpaired electrons is the most stable one in the same sublevel* **(Hund's rule).**

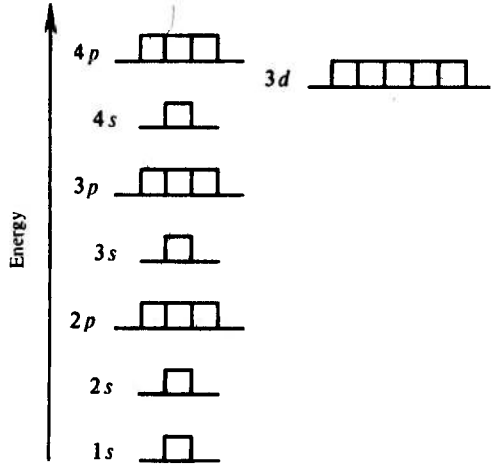


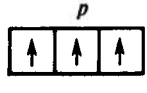
Fig. 4
Sequence of occupying the energy sublevels in an atom

Consequently, when filling the boxes, we first put one electron into each of them, after which we add the remaining electrons so as to form pairs of electrons with opposite spins. Two electrons with opposite spins in one energy state are called **paired**, while single electrons are called **unpaired**:

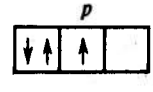


Unpaired electron Paired electrons

Hund's rule does not forbid a different arrangement of electrons in orbitals identical in their energy. It only determines the arrangement of the electrons corresponding to the normal unexcited (ground) state of an atom. For example,



Arrangement of electrons in the *p* orbitals in accordance with Hund's rule--the normal state of an atom



Arrangement of electrons in a *p* sublevel not obeying Hund's rule--a less stable (excited) state of an atom

The atomic structures of the chemical elements are considered with a view to their inseparable relation to the periodic table.

Questions and Problems

1. Proceeding from the Pauli exclusion principle, calculate the number of electrons in the fourth energy level.
2. What is the maximum number of electrons in the 3*d*, 4*d*, 5*d*, 4*f*, and 4*p* sublevels? Is the number of electrons in the sublevels related to the principal quantum number?
3. Why is it impossible for all the electrons in an atom to occupy the most profitable position from the viewpoint of energy?
4. Why can an atom never contain two absolutely identical electrons? Explain the essence of the Pauli exclusion principle.

2.5. Structure of the Periodic Table of Elements

At present, the most widespread forms of the periodic table are the short and long ones.

The short form of the table was worked out by Mendeleev in 1870 and it is called the classical form (the first variant of the table proposed by Mendeleev in 1869 had a long form, i.e. all the periods in it were arranged in one line). Each of these variants has its merits and shortcomings. For example, a substantial shortcoming of the short form is the combining of unsimilar elements in one group. A shortcoming of the long form is its lengthiness and lack of compactness. Both variants of the periodic table are given on the inside front and back covers of the book. The short form is generally studied at secondary schools, and we shall consider its structure.

Every element, depicted by its relevant symbol, has an atomic (serial) number and occupies a definite position in the table. When speaking of the place of an element in the table, we first of all have in view the general relation between it and its neighbours in the table, and through them the relation to all the other elements.

Each box in the table is the numbered position of an element in it, i.e. its coordinates.

A horizontal row of elements arranged in the order of increasing atomic numbers in which the properties of the elements change regularly from typically metallic to typically non-metallic ones and further to the noble gases is called a period.

The periodic table contains seven periods, of which the first three are called short, and the fourth, fifth, sixth, and seventh—long. The periods contain different numbers of elements. The first period contains two elements (hydrogen and helium), the second and third—eight each, the fourth and fifth—eighteen each, the sixth—thirty two, and the seventh (meanwhile incomplete) contains twenty four elements.

Each period (except for the first one) begins with an alkali metal and terminates in a noble gas. The elements of the second and third periods are called **representative**. The first period including hydrogen and helium

is distinctive. Here there is no alkali metal. How do matters stand in this period with the regular change in the properties of its elements? A glance at the table reveals that hydrogen is indicated in the first period twice, i.e. it can be considered on the one hand as an analogue of the alkali metals, and on the other as the lightest analogue of the halogens. This combination underlies the concept of the dual nature of hydrogen.

The elements of each of the first three periods are arranged in one horizontal row. The elements of each of the fourth and fifth periods are arranged in two horizontal rows. The elements of the sixth period are also arranged in this way. The seventh period (without the actinoids) meanwhile consists of one row of elements. As new elements are discovered, this period will be filled up with two rows.

The elements with atomic numbers from 58 to 71 called the lanthanoids, and with numbers from 90 to 103 called the actinoids are separated from the sixth and seventh periods. This is due to horizontal analogy explained by the structure of the atoms of these elements.

The periods are longer when they are lower in the table. The reason is that in the large periods adjacent elements are closer to each other in their chemical and physical properties than in the smaller, upper ones. In the small periods, considerable jumps in the properties are observed when going from one element to the next one. In the lower periods, on the other hand, the transition from metallic properties to non-metallic ones is slower, while there is horizontal analogy in the triads of elements forming the secondary subgroup (subgroup B) of Group VIII (for instance, the iron family Fe-Co-Ni).

The vertical columns combining elements with the same oxidation state in their higher oxides are called groups.

But there are quite a few exceptions from this rule. For example, Group I contains copper and gold, which in their higher oxides exhibit an oxidation state exceeding +1, namely, Au_2O_3 and CuO in which the oxidation states of gold and copper are +3 and +2, respectively, while Group VII contains fluorine exhibiting an oxidation state of only −1.

Not all the elements in one group are clearly similar in their properties (for example, gold and francium, copper and rubidium). Therefore, each group is divided into two subgroups—a **main** one (subgroup A) and a **secondary** one (subgroup B). The main subgroups include the elements of the small periods and those of the large periods similar to them in their properties (Group IA includes lithium and sodium, as well as potassium, rubidium, cesium, and francium).

The secondary subgroups consist only of elements of the large periods (Group IB includes copper, silver, and gold, Group IIB—zinc, cadmium, mercury, etc.).

The elements forming the main subgroups substantially differ in their chemical properties from those of the secondary subgroups. This can be illustrated by taking Groups I and VII as examples. Group VIIA contains the halogens—the most typical non-metals, whereas Group VIIB contains manganese, technetium, and rhenium exhibiting metallic properties. The differences in the properties of the elements of the main subgroups and those of the secondary subgroups within the groups first weaken when passing from Group I to Groups II and III, then grow again in Group VII. For example, if in Group I the elements of the main subgroup (the alkali metals) sharply differ from the elements of the secondary subgroups (copper, silver, gold), then all the elements of Group III are close in their properties. The metallic properties increase and the non-metallic ones diminish within the subgroups with an increase in the charge of the nucleus.

In the chemical literature, the main subgroups are generally designated by the letter A, and the secondary ones, by the letter B, as we have already mentioned. It is also general practice to denote the groups by Roman numbers. In accordance with the rules of IUPAC (the International Union of Pure and Applied Chemistry), the subgroups are also designated by a typical feature of their elements or by the name of the element having the smallest atomic number in the given subgroup. Some of the most commonly used group names are the halogens for subgroup VIIA, the alkali metals for subgroup IA, and the noble gases for subgroup VIIIA.

The periodic table of the elements reflects:

(1) the laws observed in the vertical columns (groups);

(2) the laws observed in the horizontal rows (periods) associated with the consecutive increase in the atomic number;

(3) the diagonal laws involving both the groups and periods.

Any element has properties that are intermediate between those of its two vertical or horizontal neighbours or of its neighbours along two diagonals. Consequently, the laws mentioned above allow us to compare any element with eight others.

Questions and Problems

1. List the elements of the third period. Indicate how the properties of the elements change within this period.
2. Name the elements of subgroup VA and of subgroup VIB. Use these examples to show that the metallic properties of the elements gradually grow in each subgroup.
3. Characterize the elements germanium, selenium, and phosphorus proceeding from their position in the periodic table.
4. List the elements of subgroups IIIA and IVB.
5. Indicate the number of periods and groups in the periodic table.
6. Why are the elements divided into subgroups?
7. Which elements are considered to be representative?

8. Explain the similarities and differences between elements, taking Group VII as an example.

9. The first period contains only two elements. How can one explain the regular change in the properties of the elements of this period in comparison with the second and third periods?

2.6. Electron Structure of the Atoms of the Small Period Elements

The laws manifesting themselves in changes in the properties of the elements are due primarily to the structure of the electron shells (energy levels) of the atoms. To explain these laws, let us first consider the structure of the atoms of the small period elements.

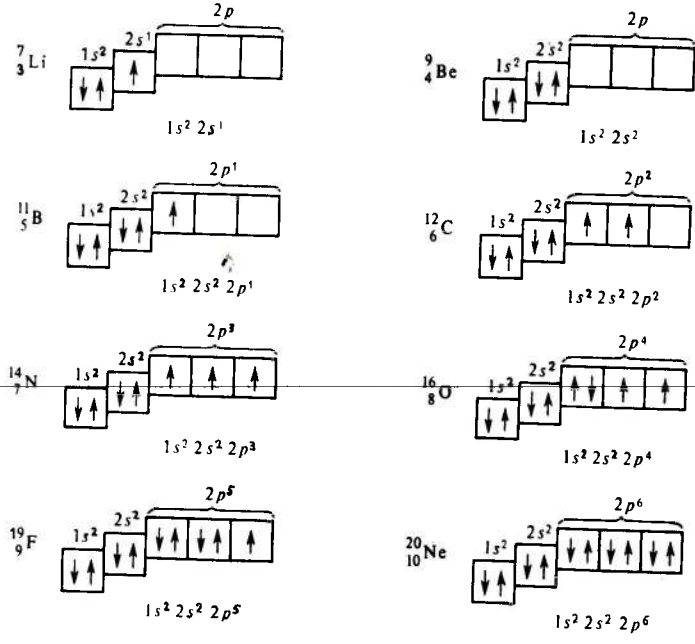
We shall begin with the first element—hydrogen. The charge of the hydrogen atom nucleus is +1. It therefore has one electron in an *s* orbital. Hence, the electron configuration of a hydrogen atom $_1H$ is $1s^1$.

The electron structures and electron configurations of the atoms of elements of the first, second, and third periods can be depicted as follows.

First period:



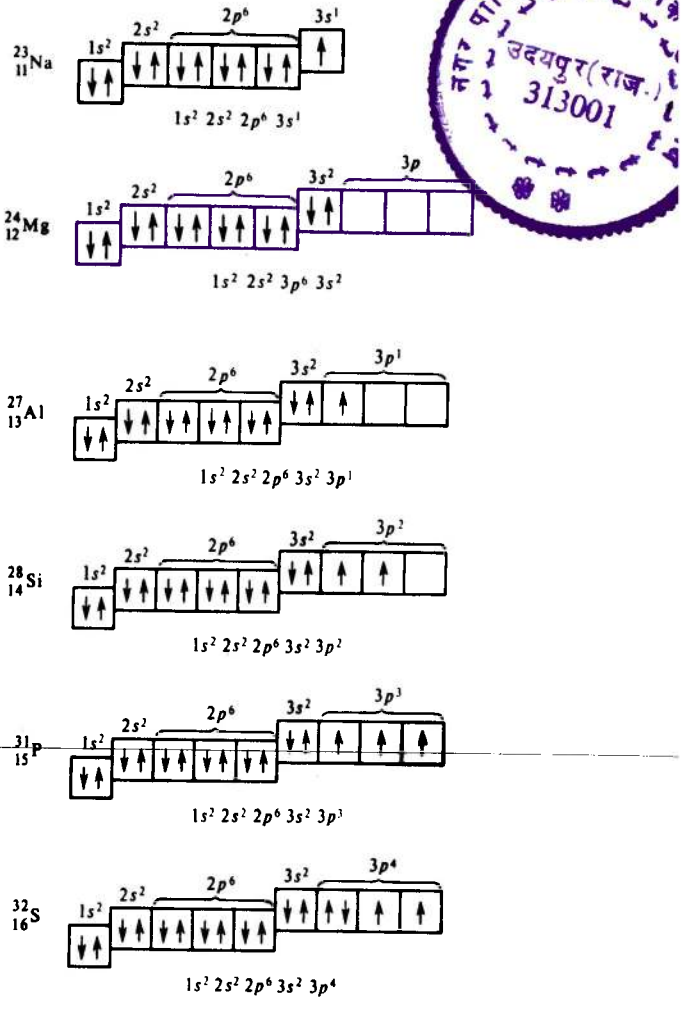
Second period:



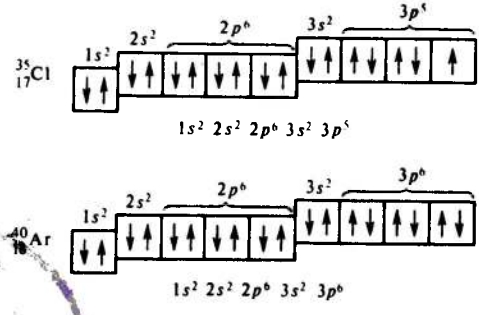
Let us stop to consider the structure of the nitrogen atom in somewhat greater detail. The three outer electrons are in the p sublevel (p^3).

For nitrogen, the distribution of the three p electrons in three $2p$ orbitals, namely, $2p_x$, $2p_y$, and $2p_z$, is the most advantageous from the energy viewpoint because these electrons have simultaneous parallel spins (identical spins) and cannot approach one another closely, which reduces their mutual repulsion.

Third period:

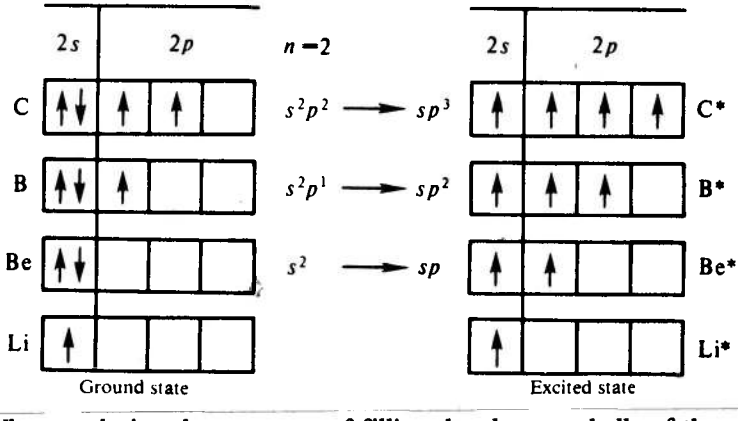


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For every atom, the above electron configurations and electron structures correspond to their **ground (normal** or **unexcited)** state, i.e. to the state of the atom with a minimal energy. Other states with a higher energy than that of the ground state are called **excited states** of the given atom. The transition of an atom from its ground state to an excited one is attended by the absorption of energy. When there are free orbitals within the limits of a given level, an electron passes from one sublevel to another one.

The following examples illustrate the transition of atoms from the ground state to an excited one:



When analysing the sequence of filling the electron shells of the atoms of the elements in the first three periods, we can see that the transition from one element to the next one within a period is attended by an increase in the number of protons in the nucleus by one. Simultaneously, every element has one more electron in its outer shell than its predecessor.

A hydrogen atom has one electron (an *s* electron). A helium atom has one electron more, i.e. its configuration is $1s^2$. These two electrons have an antiparallel spin. The first period containing two elements terminates in the noble gas helium.

The atoms of the second period elements have two energy levels (the number of the period determines the number of levels). This period begins with an alkali metal—lithium (its atomic number $Z = 3$). Two electrons of the lithium atom are in the first level. The third electron must begin the filling of the second level, therefore it is put in the box of the *s* sublevel of the second level: $1s^2 2s^1$.

The second energy level, by the Pauli exclusion principle, can accommodate a maximum of eight electrons because a *p* sublevel is also possible in addition to the *s* sublevel. Therefore the electron shells of the second period atoms are filled by from one to eight electrons. Indeed, beryllium already has two electrons in the *s* sublevel of the second level. Beginning with boron, the *p* sublevel fills (from one electron in boron to six in the noble gas neon). The second period terminates in neon ($1s^2 2s^2 2p^6$) and contains eight elements.

The third period begins with sodium ($Z = 11$). Of the 11 electrons occupying three energy levels, two are in the first level (as in helium), eight are in the second level (as in neon), while the last, eleventh electron is in the box of the *s* sublevel of the third level. Magnesium has two electrons in the box of the *s* sublevel of the third level. This level can accommodate up to 18 electrons ($N = 2n^2 = 2 \times 3^2 = 18$) because here *d* sublevels are possible in addition to the *s* and *p* ones. But since for atoms of the elements of this period the third energy level is the outer one, then by the Pauli exclusion principle it cannot have more than eight electrons, therefore with an increase in the charge of the nucleus from sodium to argon, the number of electrons in the outer level grows from one to eight.

In aluminium and all the following elements of the third period, the 3*s* orbital accommodates two electrons, therefore next the 3*p* sublevel is filled: Al—$3s^2 3p^1$, Si—$3s^2 3p^2$, P—$3s^2 3p^3$, S—$3s^2 3p^4$, Cl—$3s^2 3p^5$, and Ar—$3s^2 3p^6$. Hence, the eight elements in this period have configurations ranging from $1s^2 2s^2 2p^6 3s^1$ for sodium to $1s^2 2s^2 2p^6 3s^2 3p^6$ for argon. The third period is completed, but the third energy level is not filled up completely because *d* sublevels are possible here in addition to the *s* and *p* sublevels.

In every case, the elements of a new period as regards the structure of their inner energy levels repeat the configuration of the noble gas terminating the preceding period. This is why the following notation is often used: sodium—[Ne]$3s^1$, magnesium—[Ne]$3s^2$, aluminium—[Ne]$3s^2 3p^1$, and so on to the end of the given period.

If we compare the electron structure of atoms, we can note that the structure of the outer energy levels periodically repeats (compare lithium $2s^1$ and sodium $3s^1$, beryllium $2s^2$ and magnesium $3s^2$, boron $2s^2 2p^1$ and aluminium $3s^2 3p^1$, etc.). Such a law will also be observed in the following

periods. This is exactly what explains the periodic repetition of the properties of the elements in the periods discovered by Mendeleev, who has no information on the structure of an atom at his disposal. The theory of the structure of an atom thus confirmed the correctness of Mendeleev's discovery and supplied it with a powerful foundation.

Hence, in the small periods, the outer energy level is filled with from one to eight electrons. The levels preceding the outer ones are filled and correspond to the electron configurations of the noble gases of the previous periods.

Questions and Problems

1. Show the electron configuration of the atoms Na, Cl, Si, and F and in each of them single out the configuration of a noble gas.
2. The outer electron shell of an atom has the configuration $3s^2 3p^4$. Compile the complete electron configuration, indicate the charge of the atomic nucleus and the position of the relevant element in the periodic table.
3. What are the similar and different features of the structure of the outer energy level in silicon and carbon atoms?
4. Why are the properties of sodium and lithium similar?
5. Helium and neon are noble gases. Why is the similarity of their properties not affected by the difference in the structure of their outer level?

2.7. Structure of the Atoms of the Large Period Elements

The filling in of the energy levels in atoms of the large period elements obeys the same laws as for atoms of the small periods, but there are also important distinctions. They explain the existence of the secondary subgroups and also why there are much more elements with metallic properties in nature than with non-metallic ones.

Let us use the fourth period to see how the electron shells of atoms of the large period elements are filled. The third period terminates in argon, while the fourth one begins with potassium. It would seem that when going over from argon to potassium, the next electron should start filling in the $3d$ orbital of the third level. But potassium, the first element of the fourth period, has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, i.e. the next electron has occupied the orbital of the s sublevel of the fourth level, while the d sublevel of the third level remains unfilled. Hence, the sequence of filling is "violated" because filling in of the fourth level has begun with the third level still incomplete. This is explained by the fact that (see Fig. 4) the $3d$ sublevel has a higher energy than the $4s$ one, and therefore the $4s$ sublevel with a lower energy is filled in first because electrons always tend to fill an orbital with a lower energy.

For the same reason, the 20th electron of the calcium atom also occupies the *s* sublevel of the fourth level ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$). With an increase in the charge of the nucleus, the filling of the 3*d* sublevel (beginning with scandium) becomes more advantageous from the energy viewpoint. From scandium up to zinc inclusively, the *d* sublevel is filled with from one to ten electrons ($3d^1$-$3d^{10}$). The elements from scandium to nickel have two electrons in their outer level. Chromium is an exception—it has one electron in the outer level (an electron jumps from the 4*s* sublevel to the 3*d* sublevel). This phenomenon is called an electron jump. In the odd row of the fourth period containing the elements with atomic numbers from 31 to 36, the levels are filled somewhat differently. Here an increase in the charge of the nucleus is attended by from one to six electrons filling the *p* sublevels of the outer level (the configurations of the outer levels are $4s^2 4p^1$ to $4s^2 4p^6$ from gallium to krypton). The same building up (aufbau) order is observed for the elements of the fifth period as in the fourth one. In the atoms of the elements with $Z = 39$ to 48, the *d* sublevel of the level below the outer one is again filled from $4d^1$ to $4d^{10}$. An electron jump is observed in niobium, molybdenum, ruthenium, rhodium, and silver.

Each of the elements with atomic numbers of 39, 40, and 43 has two electrons in its outer level. A double jump occurs in the palladium atom, i.e. its outer level has no electrons. This is the only exception with such a double jump in the entire periodic table. Hence, the first two elements in the odd row of the fifth period, i.e. rubidium and strontium ($5s^1$ and $5s^2$) are followed by ten elements (from yttrium to cadmium) in which the *d* sublevels of the fourth level are filled. Cadmium is followed by six elements (indium, tin, antimony, tellurium, iodine, and xenon) in which the *p* sublevels of the outer level are built up (from $5p^1$ to $5p^6$), and the period terminates in a noble gas—xenon ($5s^2 5p^6$). These elements have 18 electrons in the level below the outer one ($4s^2 4p^6 4d^{10}$). We have again completed a period, but both the fifth and the fourth electron shells have not been filled in. In the sixth period, cesium and barium ($6s^1$ and $6s^2$) are followed by only one element—lanthanum, in which the 5*d* sublevel is filled in. After lanthanum, in the elements with $Z = 58$ to 71 (the lanthanoids), the *f* sublevels of the fourth level are filled in from $4f^2$ in cerium to $4f^{14}$ in lutecium. After lutecium, the filling in of the 5*d* sublevel from hafnium to mercury is completed. From thallium to radon, the 6*p* sublevel is filled in. The period again terminates in a noble gas ($6s^2 6p^6$).

In the seventh period (it is not complete), the electron shells are occupied similarly to the sixth period. Here two *s* elements—francium ($Z = 87$) and radium ($Z = 88$)—and one *d* element—actinium ($Z = 89$)—are followed by 14 elements called the actinoids ($Z = 90$ to 103). An increase in the atomic number of the actinoids is attended by filling in of the 5*f* sublevel.

The elements with Z = 104-107 are *d* elements. They are kurchatovium, (Z = 104), nielsbohrium (Z = 105), and elements with Z = 106 and 107, which are analogues of tungsten (eka-tungsten) and rhenium (eka-rhenium), respectively.

The electron that makes an atom of an element different from the one before it in the periodic table is called the **differentiating electron.** In other words, the differentiating electron is the last electron added in building up the periodic table.

The elements in which the differentiating electron is in an *s* sublevel are called *s* elements (they include the elements of subgroups IA and IIA). The elements in which the differentiating electron is in a *p* sublevel are called *p* elements (they include the elements of the main subgroups of Groups III-VIII). The *d* elements, in which the differentiating electron is in a *d* sublevel, include all the elements of the secondary subgroups.

The lanthanoids and actinoids are *f* elements, because the differentiating electron in them is in the *f* sublevel of the second energy level from the outer one.

It should be noted that in the building up of a *d* sublevel, the outer energy level of the atoms of *d* elements accommodates one or two electrons. It should also be noted that all these elements have sufficiently pronounced metallic properties. This allows us to draw two conclusions: first, in most cases the elements with a small number of electrons (1-3) in the outer level have metallic properties, and, second, the considerably larger number of metallic elements in comparison with non-metallic ones is explained by the larger number of *d* elements (and also *f* elements) in comparison with *p* elements.

Consequently, the beginning of a new energy level corresponds to the beginning of a new period. From the standpoint of the theory of the structure of atoms, a period can be defined as a series of chemical elements whose atoms have the same number of energy levels and are arranged in the order of the growth in the charges of the nuclei.

The elements whose atoms repeat the electron configuration of another element after a strictly definite interval form a subgroup in the periodic table.

The analogues of the small period elements form the main subgroups of the table. They are generally known as the representative elements. The major part of the remaining elements are called transition ones, and they make up the secondary subgroups.

From the viewpoint of the structure of an atom, the concepts of a group and subgroup acquire a special meaning. The studying of the properties of the chemical elements in their relation to the structure of an atom reveals that the combining of the elements into subgroups is associated primarily

with the analogy in the atomic structure. In the main subgroup elements, the analogy manifests itself in the structure of the outer energy level, while in the secondary subgroup ones it manifests itself in the structure of the outer level and the one below it. For example, in the atoms of the elements of the subgroup VIIA (the halogen subgroup)

$_{9}F—1s^2 2s^2 2p^5$

$_{17}Cl—1s^2 2s^2 2p^6 3s^2 3p^5$

$_{35}Br—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$

$_{53}I—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$

$_{85}At—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^5$

there are seven electrons in the outer level, of which two are in the *s* sublevel and five in the *p* sublevel. These elements differ in the number of their energy levels.

Within each period, the number of outer electrons in the atoms of the main subgroup elements grows each time by one from left to right as the charge of the nucleus increases, for instance:

Fourth period

$_{19}K$—1, $_{20}Ca$—2, $_{31}Ga$—3, $_{32}Ge$—4, $_{33}As$—5, $_{34}Se$—6, $_{35}Br$—7, and $_{36}Kr$—8;

Fifth period

$_{37}Rb$—1, $_{38}Sr$—2, $_{49}In$—3, $_{50}Sn$—4, $_{51}Sb$—5, $_{52}Te$—6, $_{53}I$—7, and $_{54}Xe$—8;

Sixth period

$_{55}Cs$—1, $_{56}Ba$—2, $_{81}Tl$—3, $_{82}Pb$—4, $_{83}Bi$—5, $_{84}Po$—6, $_{85}At$—7, and $_{86}Rn$—8.

Consequently, the number of outer electrons in atoms of the main subgroup elements changes periodically with an increase in the charge of the nucleus.

Let us compare the elements of the secondary subgroup of Group VII:

$_{25}Mn—1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

$_{43}Te—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2$

$_{75}Re—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^5 6s^2$

Each of these atoms has two *s* electrons in its outer level, and five electrons in the *d* sublevel of the preceding level. The difference in the structure of the elements of the given subgroup also consists only in the number of energy levels.

The similarity between the elements of a main and secondary subgroups can be traced the most clearly when comparing the second element of a main subgroup with the first element of a secondary subgroup.

Questions and Problems

1. How are the electron shells built up in atoms of the large period elements?
2. Can the above definition of a period from the standpoint of the theory of the structure of atoms be extended to the small periods?
3. A neutral atom has a set of completely built up sublevels up to 4*s*. Indicate the charge (or atomic number) of an atom of this element and its position in the table.
4. Write down and compare the electron configurations of calcium and magnesium.
5. Explain the electron configuration of bromine.
6. Why are there many more elements with metallic properties than with non-metallic ones?
7. How can one explain the similarity of the properties of the elements in one subgroup. Give examples.

2.8. Relation between the Properties of Elements and Their Position in the Periodic Table

The features of the electron structure of atoms determine the laws of the change in the properties of the elements in the periodic table.

Properties of the elements such as their atomic radii, ionization energies, electron affinity, electronegativity, and oxidation state depend first of all on the structure of the outer electron shells, consequently, the periodic change in the electron structure of atoms determines the periodic change in these properties. This is the physical meaning of Mendeleev's periodic law.

Quantum mechanics teaches that an isolated atom cannot have a strictly definite size. On the one hand, the electron cloud actually becomes very blurred already at a distance of a few nanometres from the nucleus, while on the other, the electron density theoretically shrinks to zero only at an infinitely great distance from the nucleus. Hence, it is practically impossible to determine the absolute sizes of atoms. We can only speak of the radii determined from the internuclear distances in solid substances and gaseous molecules (the **effective radii of atoms**).

It is possible to determine the orbital radii of atoms: they are the distance from a nucleus to the remotest maximum of the electron density. Any atom in the ground state can have one value of the orbital radius, whereas in excited states it can have many values of it. The **orbital radii of atoms**, like their effective radii, are in a periodic relation to the charge of the nucleus (Figs. 5 and 6). The atomic radii are the largest at the beginning of a period, and then diminish somewhat along it. This is associated with the consecutive increase in the charge of a nucleus and, accordingly, in the number of electrons. When going over to a new period, the radius again grows sharply because a new energy level has appeared. Consequently, the atomic radius grows with an increase in the principal quantum number n.

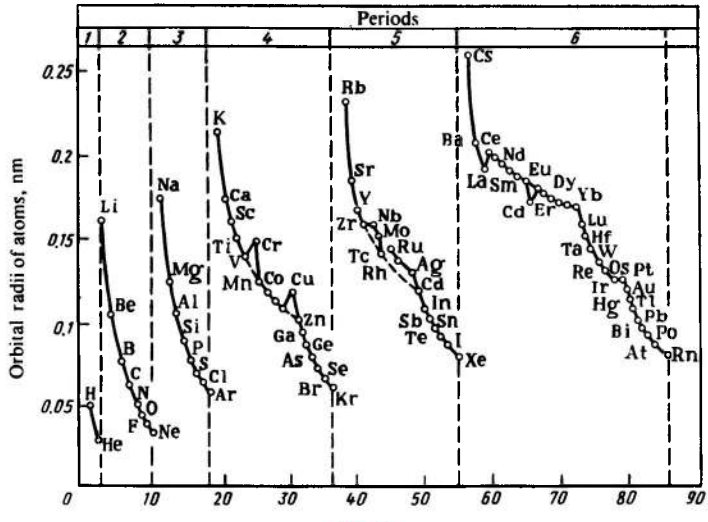


Fig. 5

Dependence of the orbital radii of atoms on the atomic numbers of the elements

In the elements of one group, the atomic radii consecutively grow with an increase in the nuclear charge (atomic number). The ions formed by atoms losing their electrons (cations) have a smaller radius than the parent atoms. If an ion is formed by the gaining of an electron (an anion), its

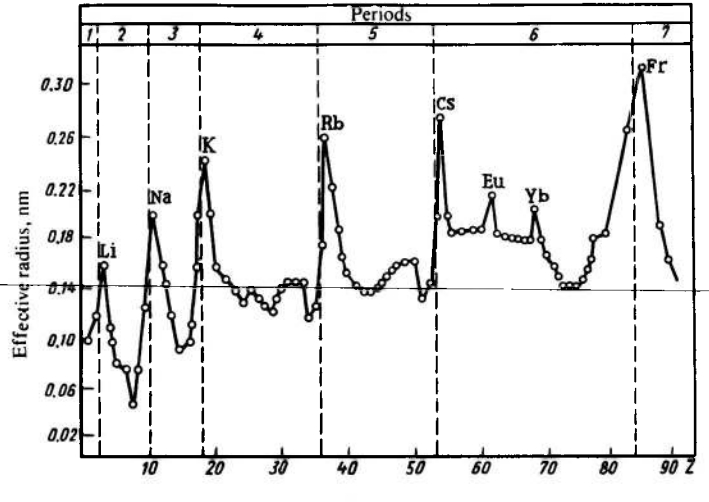


Fig. 6

Dependence of the effective radii of atoms on the atomic numbers of the elements

radius is larger than that of the parent atoms. In elements belonging to one period, the radii of cations are smaller than those of anions:

$$r(\mathrm{Li}) = 0.155 \text{ nm} \quad r(\mathrm{F}) = 0.064 \text{ nm}$$
$$r(\mathrm{Li}^+) = 0.060 \text{ nm} \quad r(\mathrm{F}^-) = 0.136 \text{ nm}$$

Within a group, the ionic radius grows with an increase in the nuclear charge.

An important characteristic of an atom determining its ability to give up an electron is its **ionization energy** (or **ionization potential**). It is the amount of energy needed to remove an electron from an atom and transform the latter into the relevant ion.

In chemical investigations, the first ionization energy, i.e. the energy needed to completely remove the first electron from an electrically neutral atom, is of paramount importance. This corresponds to the process described by the equation

$$\text{atom} + \text{energy (IE)} \rightarrow \text{positive ion} + e^-$$

The ionization energies grow across each period (Fig. 7). Here an alkali metal has the smallest ionization energy, and a noble gas—the largest energy.

The ionization energy decreases in a group with a growth in the charge of a nucleus. As already indicated, the elements of one group have the same configuration of their outer electron shells, but differ in the values

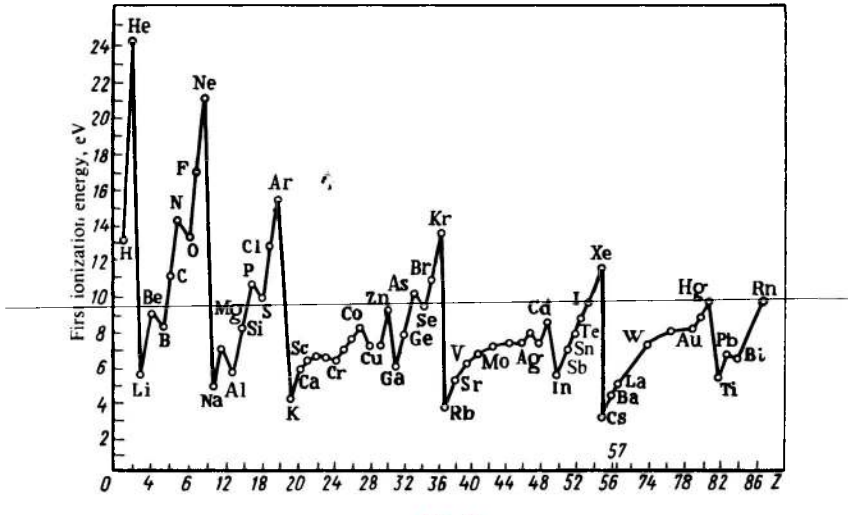


Fig. 7

Dependence of the ionization energies of atoms on the atomic numbers of the elements

of the principal quantum number (the elements are in different periods). When going down a subgroup, the atomic radii of the elements grow, hence the attraction of an electron to a nucleus weakens, and it becomes easier to remove an electron.

Consequently, the outer electrons in unfilled outer levels or in the ones next to them are responsible for the interaction of atoms with one another (for instance, the formation of a chemical bond, and the transfer of electrons).

Another important property also determined by the electron structure of the outer shells is the **electron affinity** (EA). Atoms can not only lose electrons, but can also gain them, which can be shown by the equation

$$\text{atom} + e^- \rightarrow \text{negative ion} + \text{energy (EA)}$$

The energy evolved when an electron is attached to a free atom is called the **electron affinity.**

The latter is a periodic property. It grows across a period, reaching a maximum in the halogens. The latter, as we know, have a configuration of their outer shells of ns^2np^5. The transition from a halogen to a noble gas leads to the configuration ns^2np^6, which is completely filled. This is why the atoms of the noble gases do not attach electrons. The opposite relation is observed down a subgroup, i.e. the electron affinity diminishes with an increase in the nuclear charge.

The ionization energy and electron affinity are important characteristics of the reactivity of the atoms of an element. If the atoms of two elements differ greatly from each other in the values of the ionization energies, then one of them will have a low ionization energy, and the other—a high electron affinity. Such atoms will readily react with each other and form a stable bond. The practical use of these characteristics is limited by the fact that they relate to isolated atoms, i.e. to gaseous states. If atoms are not isolated, however, another characteristic is customarily used known as the **electronegativity**, i.e. the ability of an atom to attract electrons that are shared when a chemical bond forms. A measure of electronegativity is the energy equal to the arithmetic sum of the ionization energy I and the electron affinity E, namely, $EN = I + E$.

More frequently, however, values of the relative electronegativity are used. In this case, a value of 4.00 is assigned to fluorine, which is the most electronegative element, and the other elements are considered relative to it (Table 2).

The electronegativity gradually grows across a period—the alkali and alkaline-earth elements have the smallest values, and the halogens have the greatest ones. When the electronegativity of an element is higher, its nonmetallic properties are more pronounced.

Table 2

Relative Electronegativities of Selected *s* and *p* Elements

			H 2.1			
Li 0.97	Be 1.47	B 2.01	C 2.50	N 3.07	O 3.50	F 4.00
Na 1.016	Mg 1.23	Al 1.47	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.91	Ca 1.04	Ga 1.82	Ge 2.01	As 2.20	Se 2.48	Br 2.74
Rb 0.89	Sr 0.99	In 1.49	Sn 1.72	Sb 1.82	Te 2.01	I 2.21

The electronegativity decreases down a group, and the metallic properties of the elements grow (Fig. 8).

Most elements are metals, they are in Groups I and II, and also form the secondary subgroups of Groups III-VIII. Important features of metallic elements are that they have one, two or three electrons in their outer energy level, and also have low values of their ionization energies and electronegativity. This is why metals tend to give up electrons.

The non-metallic elements differ from the metallic ones in having higher values of the ionization energy, electron affinity, and the electronegativity.

The atomic radii of non-metals diminish across a period. A non-metal has four, five, six, seven, or eight electrons in its outer shell.

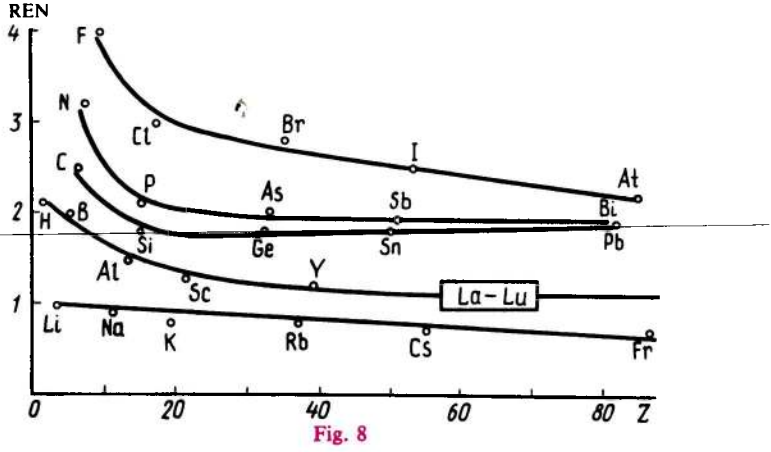


Fig. 8

Dependence of the relative electronegativity (REN) of elements on the nuclear charge of their atoms

Questions and Problems

1. How do the atomic radii of elements change down a subgroup? Across a period? Why?
2. Explain the concepts of ionization energy, electron affinity, electronegativity, and show how they are related to one another.
3. What is the relation between an atomic radius and the ionization energy?
4. How do the properties of an element depend on the number of the period which it is in?
5. What is meant by "the metallic properties of a chemical element", and "the non-metallic properties of a chemical element"?
6. Name the most electronegative element. Defend your answer.
7. Why does the electronegativity grow across the periods and decrease down the groups?

2.9. Analysis of the Properties of Elements, Their Oxides and Hydroxides

Metals as simple substances are characterized by their electrical conductance, thermal conductance, metallic lustre, ductility, and plasticity. The metallic properties are most pronounced in the simple substances formed by the elements in the left bottom corner of the periodic table.

The number of metallic elements within a period grows down the periods (Fig. 9). For example, the second period contains only two metals, the third one—three, and the fourth one—thirteen. The metallic properties of the elements attenuate across the periods, i.e. the ability of the elements to lose electrons weakens and the ability to gain electrons grows.

The elements in the right upper part of the table are non-metals.

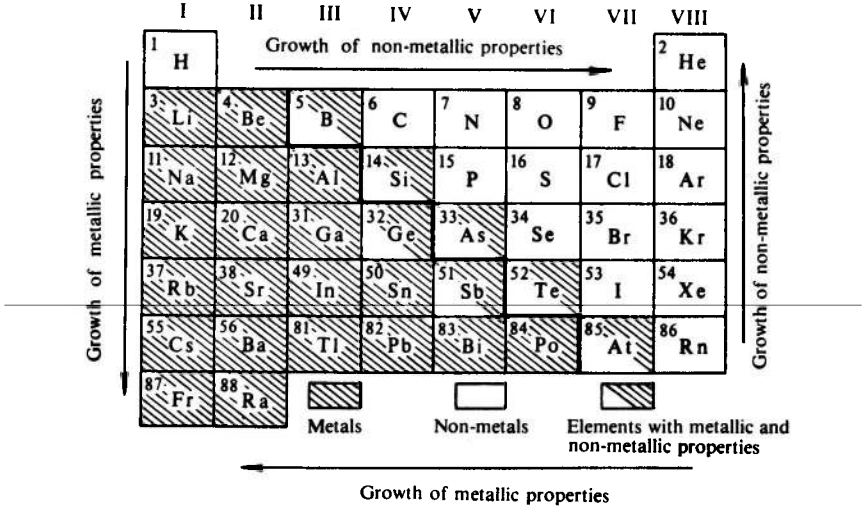


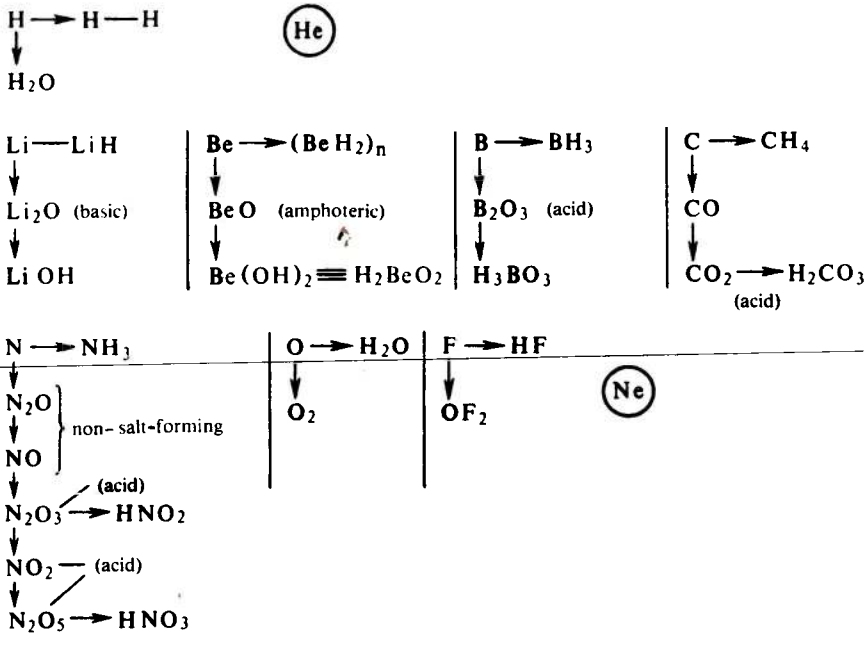
Fig. 9
Elements with metallic and non-metallic properties

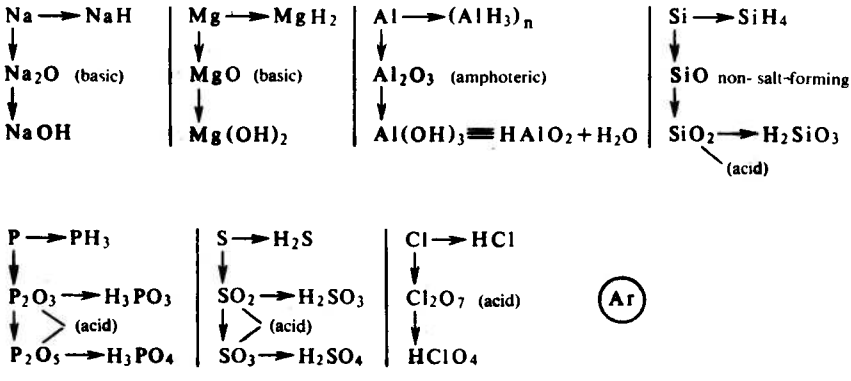
The noble gases (He, Ne, Ar, Kr, Xe, and Rn) have eight electrons in the outer shell of an atom with the configuration ns^2np^6, therefore they are monatomic in the form of simple substances. The halogens, nitrogen, oxygen, and hydrogen exist as simple substances in the form of diatomic molecules. Unlike metals, non-metals conduct heat and electricity poorly, or do not conduct them at all. The non-metals except for those indicated above can exist at standard temperature and pressure in either the crystalline or amorphous state.

The metals can be separated from the non-metals by a diagonal line in the periodic table drawn from boron to astatine. This boundary can be depicted quite easily in the long-period variant of the table (see the back inside cover). Elements exhibiting properties of both metals and non-metals are along this boundary. They include boron, silicon, germanium, arsenic, antimony, tellurium, and astatine, which are combined under the name semimetals (metalloids).

Hence, each period has, as it were, a "boundary zone" accommodating an element exhibiting dual properties the most prominently. Consequently, the transition from a typical metal to a typical non-metal in each period occurs gradually: first typical metallic properties prevail, and at the end, non-metallic ones. In the large periods, this transition is still more gradual.

Let us analyse the properties of the hydrogen and oxygen compounds of the elements by periods:





A comparison of the properties of simple substances, and also of the hydrogen and oxygen compounds of the elements, allows us to draw the following conclusions:

(1) the properties of simple substances change from metallic to non-metallic;

(2) the elements (except for helium, neon, and argon) form hydrogen and oxygen compounds whose physical properties change from solid to gaseous ones (LiH and NaH, BeH_2 and MgH_2 are solid hydrides; CH_4 and SiH_4, NH_3 and PH_3 are gaseous hydrogen compounds; Li_2O and Na_2O, BeO and MgO are solid oxides; CO_2, NO_2, SO_2 are gaseous oxides);

(3) the hydrogen compounds change from solid to volatile ones; the properties of oxides and hydroxides change from basic to acidic via amphoteric ones both across the periods and down the groups. The basic nature of oxides and hydroxides gradually weakens across a period and gives way to amphoteric properties. The acidic properties increase toward the end of a period. Each period begins with an element whose oxide and hydroxide have pronounced basic properties and terminates in an element whose oxides and hydroxides with the highest oxidation state of the central atom are strong acids.

The basic nature of oxides and hydroxides grows and their acidic properties weaken down each main subgroup (except for Group VIII).

The main subgroups of Groups II-VI also contain elements whose oxides have amphoteric properties. How the properties of oxides and hydroxides change are shown in Fig. 10 for the elements of the main subgroups.

A comparison of all the data on the structure and properties of the atoms of the chemical elements allows us to conclude that *the atomic number is the main characteristic of an element.* It determines all the other properties

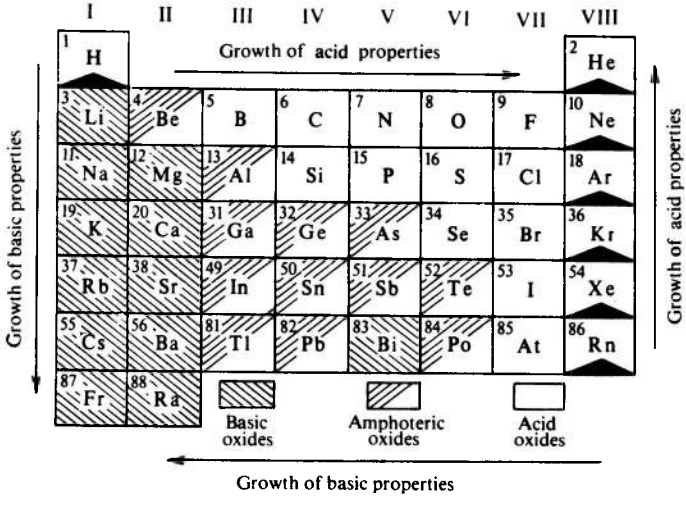


Fig. 10
Change in the properties of oxides and hydroxides in the main subgroup elements

of an element. In this connection, the periodic law with a view to the structure of an atom is formulated as follows:

the properties of the elements and of their compounds depend periodically on the charge of the nucleus (the atomic number).

Questions and Problems

1. How is the growth in the non-metallic properties across a period related to the change in the number of electrons in the outer energy level?
2. Which element has more pronounced metallic properties—arsenic or phosphorus?
3. Name the most active metal and most active non-metal, knowing the laws of the changes in the properties of elements in the groups and periods.
4. Explain what is meant by periodicity.
5. How does the highest oxygen state of elements change in the small and large periods?
6. An element is in the fourth period and Subgroup VIA. Using these data, compile the chemical formulas of the hydrogen compound and higher oxide of this element.
7. How do the properties of simple substances change within periods and within groups?
8. Give examples of how the properties of an element affect the properties of the simple substance formed by this element.
9. Confirm by examples how the properties of an element affect the properties of its hydrogen compounds.
10. The properties of oxides and hydroxides of various elements change within a period. Show the laws of these changes taking the third period as an example.
11. Find the place of gallium in the periodic table. Predict the chemical formula of its oxide and hydrogen compound.
12. Where is the boundary between metals and non-metals? Which elements are conditionally called semimetals?

2.10. Significance of the Periodic Law

The scientific significance of the periodic law extends far beyond the confines of chemistry. Being an objective law of nature, the periodic law has tremendously affected the development of many fundamental sciences and resulted in the appearance of new branches of chemistry.

When working on the periodic table, Mendeleev predicted the existence of eleven new elements. The accuracy of this prognosis depended primarily on how far the elements surrounding the unknown one had been studied. This approach was brilliantly confirmed with the discovery of gallium, scandium, and germanium.

Almost 100 years before their discovery, Mendeleev was able to predict the existence of the transuranium elements. The entire time following the discovery of the law was only a practical confirmation of Mendeleev's predictions.

The discovery of the periodic law triggered a scientifically substantiated method of the directed search for new chemical elements. The numerous achievements of modern nuclear physics can serve as examples. Only during the last 20 years were elements with the atomic numbers from 102 to 110 synthesized in the USSR. The studying of their properties, like their preparation, would be impossible without a knowledge of the laws underlying the relations between the chemical elements.

The periodic law and periodic table of the elements reflect the laws of nature. When analysing the properties of the elements, we see that they are related by the common nature of their structural features. For instance, the electron configuration s^2p^5 corresponds to the outer energy level of the halogens, which indicates their high electronegativity, minimal atomic radii, high ionization energies, etc.

It should also be noted that the discovery of the periodic law was the beginning of fundamental research relating to the properties of matter.

As aptly noted by Niels Bohr, the periodic table is a guiding star for research in the field of chemistry, physics, mineralogy, and engineering.

SUMMARY

You have become acquainted with the structure of the periodic table of the elements and modern notions on the structure of an atom. The relation between the structure and properties of chemical elements has been considered in accordance with their location in the periodic table.

The most important characteristic of an atom is its atomic number.

The modern theory of the structure of an atom proceeds primarily from the notions of the dual particle and wave nature of an electron and

describes its state by four parameters—quantum numbers. The maximum number of electrons that can occupy one orbital is two, which corresponds to the Pauli exclusion principle. Electrons occupy the same orbitals so that their total spin is maximum.

Energy sublevels whose number is determined by the principal quantum number correspond to each energy level.

The structure of the electron shells of atoms corresponds strictly to the position of an element in the periodic table. This is why the periodic repetition of the properties of the elements depends on the periodic repetition of the electron structures of the relevant atoms. The properties involved here include the atomic radius, ionization energy, electron affinity, electronegativity, and oxidation state.

The properties of simple substances, as well as of oxides and hydroxides, also depend on the position of an element in the table. All these laws witness that the periodicity in the repetition of the properties of elements depends on the charge of their atomic nuclei.

CHAPTER 3

CHEMICAL BONDS AND THE STRUCTURE OF MOLECULES

OBJECTIVES

To explain why some atoms react with each other to form molecules (for instance, $Cl + Cl = Cl_2$), whereas others do not (for instance, the reaction $He + He = He_2$ is impossible); to explain why atoms when reacting with one another combine in strictly definite proportions and in a definite sequence; to show the relation between the nature of a bond and the geometry of a molecule.

3.1. Covalent Bond

A chemical bond is the set of forces acting between atoms or a group of atoms. Molecules form as a result of the action of these forces.

The term **valence** is generally used when discussing a chemical bond. This term signifies *a measure of the ability of an element to form a chemical bond.* A chemical bond mainly forms at the expense of what we call valence electrons. In *s* and *p* elements, the electrons of the outer shell are the valence ones, while in *d* elements the *s* electrons of the outer shell and the *d* electrons of the one below it are the valence electrons.

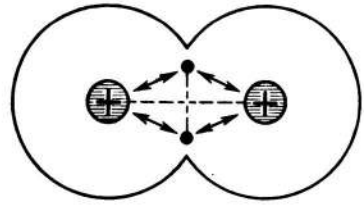


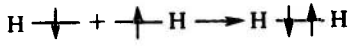
Fig. 11
Interaction in a system comprising two hydrogen atoms

To describe a chemical bond means to see how the electron density is distributed in a molecule. Depending on this distribution, we distinguish three main types of chemical bonds, namely, a **covalent, ionic** and **metallic** ones.

Let us consider the formation of a covalent chemical bond between two hydrogen atoms (H_a and H_b). When hydrogen atoms approach each other, various kinds of interaction occur: repulsion between the nuclei, repulsion between the electrons, and attraction of each of the electrons to the nuclei. Consequently, for a molecule of H_2 to exist, the forces of attraction and repulsion must balance each other. Under this condition, mutual overlap of the atomic orbitals with antiparallel spins of the electrons occurs. An increased electron density appears in the region of overlap, which is between the nuclei. It attracts both nuclei of the hydrogen atoms. The result is the formation of a sufficiently stable molecule because such a state corresponds to a minimum of energy and a definite bond length (Fig. 11).

The two bonding electrons in the H_2 molecule are in a definite region surrounding the two nuclei, and a molecular electron cloud forms. The formed molecular orbital is characterized by a lower energy level than the initial atomic orbitals. The two electrons retained together by these nuclei form a chemical bond between the two hydrogen atoms.

Thus, each of the joining atoms supplies one electron to form the pair of electrons responsible for the covalent bond. The unpaired electrons forming the pair of electrons common for two atoms are said to be **shared**, and this pair of electrons is called the **shared pair**. This can be depicted schematically as follows:



or

$$H\cdot + \cdot H \longrightarrow H : H$$ (electron dot formula of H_2 molecule)

A chemical bond produced by the formation of electron pairs shared by the interacting atoms is called a covalent bond.

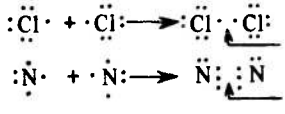
A covalent bond in other molecules is formed in the same way as in a hydrogen molecule. A pair of electrons is needed for each bond, consequently two unpaired electrons are needed—one from each atom.

The joining atoms build their outer electron layers up to eight-electron ones (or a two-electron one as in hydrogen).

A different number of covalent bonds can form in molecules between two atoms. Let us consider as an example the formation of the molecules Cl_2 and N_2. The outer shell of a chlorine atom has seven electrons, and of a nitrogen one has five. A chlorine atom has one unpaired electron and a nitrogen atom has three:



The dots adjoining the symbol of a chemical element show the number of electrons in its outer shell. The formation of the molecules Cl_2 and N_2 can be represented as follows:



A glance at the above diagram reveals that a chlorine molecule has only one shared pair of electrons, while a nitrogen molecule has three. Each atom reaches the electron configuration of a noble gas atom.

When comparing the covalent bonds between the atoms in molecules of simple substances, we can note the same law; the electrons take up a position between the nuclei of two atoms, neutralize the repelling action of the positive charges of the nuclei and bind them into a single molecule—H_2, Cl_2, N_2, etc. If molecules are formed by like atoms, the shared electron pair will not be pulled over to one side. Each pair of electrons will consequently belong equally to two atoms. This signifies that the centre of gravity of the paired electron cloud will be arranged symmetrically between the centres of gravity of the positive charges of both nuclei. Hence, the shared electron pairs will be at the same distance from the nuclei.

A bond formed by a pair of shared electrons belonging equally to both joined atoms is called a **non-polar covalent bond**. All like atoms or atoms with very close values of their electronegativity are bonded in this way (Fig. 12).

If the electronegativity of the atoms forming a molecule is not the same, the bonding pair of electrons is displaced from its symmetrical position

* The formation of an oxygen molecule O_2 must never be explained in this way. Its structure lends itself with difficulty to a description by the method of valence bonds we are using. The method of molecular orbitals, which it is better to use in this case, is studied only at higher educational establishments.

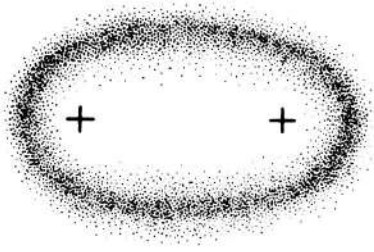


Fig. 12
A non-polar covalent bond

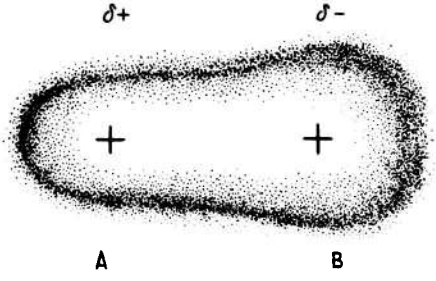


Fig. 13
A polar covalent bond

in the direction of the atom with the higher electronegativity. Consequently, the electron pair becomes pulled back to some extent by one of the combining atoms. The orbitals of the electrons of this pair remain bonded to both nuclei. As a result of such partial displacement, called **polarization**, the centres of gravity of the electric charges in the molecule will not coincide, and a certain distance will appear between them. Such a covalent bond is called **polar** (Fig. 13), and the molecule is called a **dipole**.

When the length of a dipole is greater, the polarization and polarity of a molecule are higher.

A polar covalent bond is typical, for example, of molecules such as H_2O, H_2S, HCl, N_2O_5, and of all the acids.

Questions and Problems

1. How does a non-polar covalent bond form in a chlorine molecule?
2. Why does a polar bond appear in a hydrogen chloride molecule?
3. How can you explain the formation of polar molecules of substances?
4. What is the valence of chlorine in a chlorine molecule? And in a hydrogen chloride molecule? Defend your answer.
5. In what does a molecular orbital differ from an atomic one?
6. Why is a diatomic hydrogen molecule more stable than a separate hydrogen atom, while helium, conversely, is stable in the monatomic state?

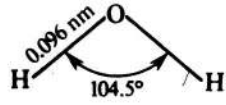
3.2. Properties of a Covalent Bond

The important characteristics of a covalent bond affecting the properties of the relevant substance include the length, energy, saturation, direction, polarity, polarizability of the bond, the bond angle, and the hybridization of the orbitals.

These characteristics will help one understand the properties of both inorganic and organic substances.

The internuclear distance between chemically bound atoms is called the **bond length**. For instance, in an H_2O molecule, the distance between the

atomic nuclei of hydrogen and oxygen is 0.096 nm. The angle between imaginary lines passing through the nuclei of two atoms and the nucleus of a central atom chemically bound to them is called the **bond angle**. In a water molecule, this angle is 104.5°:



The strength of a bond is measured by the **bond energy**, which is the amount of energy necessary to break a bond, or the gain in energy when a molecule forms from separate atoms. For example, the energy of the H—H bond in an H_2 molecule is 435 kJ/mol, and that of the F—F bond in an F_2 molecule is 159 kJ/mol. This energy for a nitrogen molecule is 940 kJ/mol. These examples show that in the formation of one mole of H_2, F_2, and N_2 from isolated atoms, the amount of energy evolved is 435, 159, and 940 kJ, respectively. The same amount of energy should be absorbed when one mole of these simple substances decomposes into isolated atoms (the atomization energy of a molecule).

Saturation is the property of atoms to form a strictly definite number of covalent bonds. For instance, the chemical bond in a hydrogen molecule is formed by a pair of electrons having opposite spins. The joining of a third atom to an H_2 molecule is impossible because its spin would coincide with that of one of the two electrons in the diatomic molecule.

Consequently, the chemical bond in an H_2 molecule is formed by a pair of electrons having opposite spins. A covalent bond in other molecules (for example, N_2, HCl, and H_2O) is formed by a pair of atoms each giving up one unpaired electron. Consequently, if an atom has n unpaired electrons, it can form covalent bonds with n other atoms each having one unpaired electron. There is thus a direct relation between the valence and the number of unpaired electrons*.

Since orbitals differ in their symmetry, they can overlap in different ways, and this is just what determines the direction of covalent bonds in space. This property of a covalent bond determines the geometry of molecules (their space structure). Depending on how the orbitals overlap and on the symmetry of the formed electron cloud, we distinguish sigma (σ) and pi (π) bonds. Let us consider some examples.

* To determine the valence of an element, it is necessary to take account not only of the ground state of an atom, but also of its excited state. This can be illustrated taking as examples elements of the second and third periods. For instance, in the ground state, the electron configuration of the outer shell of a carbon atom is $2s^2 2p^2$. When one of the $2s$ electrons is excited to a free $2p$ orbital, the number of unpaired electrons in the outer shell grows to four.

When considering the covalent bond in a hydrogen molecule, we showed that it is formed by the overlap of spherical symmetrical *s* orbitals (*s-s* interaction).

Atoms with *s* valent electrons can form simple bonds in any direction in the same way, and all the directions will be equivalent.

In HCl, the covalent bond is formed with the overlap of the *s* orbital of the hydrogen atom and one *p* orbital of the chlorine (*s-p* interaction). The molecule has a linear shape.

In a water molecule, each of the two unpaired 2*p* electrons of oxygen interacts with an *s* electron of a hydrogen atom. The orbitals of the 2*p* electrons of oxygen are perpendicular to each other, hence it should be expected that with the maximum overlap, the bond angle between the bonds should be 90°. But the experimentally found bond angle between the bonds is 104.5°. This deviation can be explained by the mutual repulsion of the hydrogen atoms not directly bonded to each other. Molecules like water are called V-shaped.

In an NH_3 molecule, the three covalent bonds are formed by the overlap of three 2*p* orbitals of the nitrogen atom and the *s* orbitals of the three hydrogen atoms. The bonds are arranged along the three axes of the *p* orbitals, therefore the molecule has a pyramidal shape with the nitrogen atom at the apex and the hydrogen atoms forming the triangular base.

Covalent bonds formed by the **direct** or **head-on** overlap of orbitals (i.e. along the bond axis—the line passing through the centres of the nuclei of the interaction atoms) are called sigma bonds. Figure 14 shows how sigma bonds form in the interaction of two *s* (a), an *s* and *p* (b), and two *p* orbitals (c).

If covalent bonds form by the **sideways** overlap of orbitals (i.e. at both sides of the bond axis), they are called pi bonds (Fig. 14d).

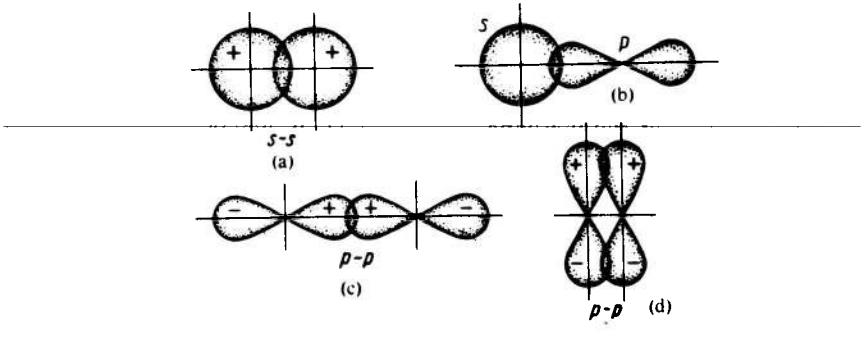


Fig. 14

Overlap of orbitals in the formation of sigma and pi bonds

Electron *s* orbitals can participate only in sigma bonds, while *p* electrons can participate in sigma and pi bonds.

If atoms in a molecule are joined by a double or triple bond instead of a single one, only one of them is a sigma bond.

Of the three bonds in the nitrogen molecule N≡N, one is a sigma bond (p_x—p_x) and two are pi bonds (p_z—p_z and p_y—p_y).

Since electrons in various energy states participate in the formation of bonds between atoms, the question arises about the equivalence and strength of these bonds. For example, a beryllium atom in the excited state ($1s^2 2s^1 2p^1$) has two unpaired electrons in its outer shell. It ought to be expected that the bonds are not equivalent in the molecule $BeCl_2$ because one of them forms owing to the interaction of the 2*s* electron of beryllium with the 3*p* electron of one chlorine atom, while the second bond forms because of the interaction of the 2*p* electron of beryllium with the 3*p* electron of the second chlorine atom. Experimental data show, however, that the bond angle in $BeCl_2$ is 180°, i.e. the molecule is linear and both bonds have the same strength.

An excited carbon atom ($1s^2 2s^1 2p^3$) has one 2*s* electron and three 2*p* electrons, but all four bonds in the molecule CCl_4 are equivalent and the bond angle is 109.5°. That electrons not equivalent in their initial state form equivalent bonds may seem to be contradictory. To explain these facts, L. Pauling introduced the concept of the **hybridization of orbitals**, according to which chemical bonds are formed by electrons not in "pure", but in "mixed" or hybrid orbitals.

Hybridization is the blending of atomic orbitals with different (but close) energy states as a result of which the same number of orbitals appear identical in their shape and energy.

In hybridization, the initial shape and energy of the orbitals change, therefore the formed hybrid orbitals differ from the initial ones. Figure 15 shows various types of atomic orbital hybridization.

A bond formed by electrons in hybrid orbitals is much stronger than an ordinary bond because overlap occurs to a greater extent than when non-hybrid orbitals participate.

Let us consider the methane molecule CH_4 in which a chemical bond forms at the expense of hybrid orbitals. It has been shown above that when one electron of a carbon atom is excited from the state 2*s* to the state 2*p*, four unpaired electrons form and four hybrid orbitals correspond to them. Consequently in the given case, the combination of one *s* and three *p* orbitals leads to sp^3 hybridization. The hybrid orbitals are directed symmetrically at an angle of 109°28′, which corresponds to a tetrahedral shape. The overlap of the hybrid orbitals with the 1*s* orbitals of the hydrogen atoms produces the tetrahedral molecule of methane (Fig. 16).

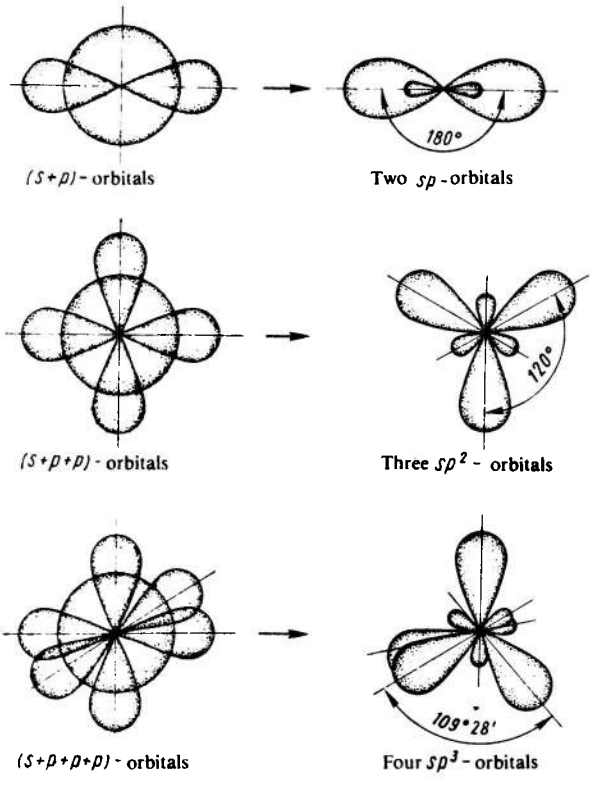


Fig. 15
Hybridization of valence orbitals

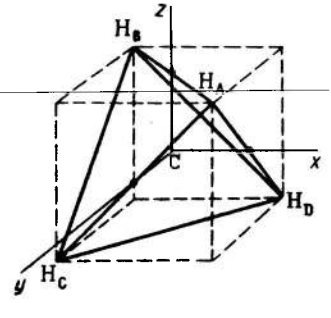


Fig. 16
Arrangement of atoms in a CH_4 molecule

The compounds CCl_4, CF_4, NH_4^+ and others have a similar structure.

We have already learned that polarity manifests itself when a covalent bond forms between atoms with a different electronegativity. Here we must distinguish between the polarity of a bond and the polarity of a molecule. Not any polar bond causes a polar molecule to form. The diatomic molecules of compound substances such as HCl, HBr, and CO are always polar. Sometimes the manifestation of polarity requires that the centres of distribution of the positive and negative charges should not coincide. In a CO_2 molecule, the carbon-oxygen bonds are polar; the carbon atom carries a positive charge, while each of the oxygen atoms carries the same negative charge. Consequently, the centre of the positive charge is concentrated on the carbon atom. Since the oxygen atoms are on one straight line at both sides of the carbon atom (the molecule is linear) at equal distances from it, the positive charge is neutralized. Hence, notwithstanding the polarity of each bond in CO_2, the molecule as a whole is not polar, and this is due to its linear structure. Conversely, the molecule H—C≡N is polar because the carbon-hydrogen and carbon-nitrogen bonds are of a different length and a different polarity.

The polarity and polarizability of a bond should be distinguished.

The **polarizability of a bond** is its ability to become polar or still more polar. This process occurs either under the action of an external electric field or under the influence of another molecule that is a partner in a reaction. These effects may result in polarization of a bond attended by its complete breaking. The bonding pair of electrons remains in the more electronegative atom, which causes the formation of unlike ions. This kind of bond breaking is called heterolytic*. For example:

$$H : \ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow H^+ + :\ddot{\underset{\cdot\cdot}{Cl}}:^-$$

Bonding electron pair

Owing to such an asymmetrical breaking of the bond, an H^+ ion forms and the chlorine transforms into the anion Cl^-.

In some molecules with covalent bonds, the joining atoms supply different numbers of electrons for the formation of bonds. This is why the numerical value of the valence fails to coincide with the number of unpaired electrons. Such a lack of agreement is observed when one of the interacting atoms has its pair of electrons, while the other has a free orbital, in other words, one atom has an unshared pair of electrons, while the second one

* Besides heterolytic bond breaking, symmetrical breaking is possible when each of the formed particles contains an unpaired electron. This kind of bond breaking is called homolytic:

$$H : H \longrightarrow H\cdot + H\cdot$$

has vacant orbitals. Let us see how ammonia reacts with hydrogen chloride:

$$NH_3 + HCl = NH_4Cl$$

or

$$\ddot{N}H_3 + H^+ \longrightarrow \left[\begin{matrix} H \\ \ddot{N}H_3 \end{matrix}\right]^+$$

Nitrogen's unshared pair of electrons migrates to the hydrogen ion H^+ (a proton) that has a vacant 1*s* orbital. The nitrogen atom being the supplier of a two-electron cloud is called a **donor**, while the H^+ ion having a free vacant orbital and receiving this electron pair is called an **acceptor**. Hence, the donor's electron pair is now shared between the donor and acceptor. This mechanism of covalent bond formation is called a **coordinate covalent** or **dative bond**.

In the formed ammonium ion, the number of electrons belonging to the nitrogen atom is less by one than in the unbonded atom. It is charged positively, and the valence state is similar to that of carbon in methane.

The N—H bonds formed by various mechanisms are equivalent in their characteristics.

Questions and Problems

1. Explain what determines the internuclear distance. Why do the nuclei of atoms fail to merge when atoms approach one another?
2. Depict all the possible ways of the overlap of an *s* orbital with a *p* orbital, and of two *p* orbitals. Indicate the direction of the bond, and also indicate sigma and pi bonds.
3. Why is the use of hybrid orbitals preferable to conventional ones (non-hybridized) in the formation of a chemical bond?
4. Write the electron configurations of the ground and excited states of B, Si, and P atoms.
5. Predict the geometry of the molecules CF_4, SiH_4, and PH_3.
6. Does analogy exist in the structure of the molecules H_2O and H_2S, PH_3 and NH_3, LiCl and HCl? Defend your answer.
7. Explain the dative mechanism of a covalent bond using the example of the formation of a phosphonium ion $[PH_4]^+$.
8. Determine the relation between parameters such as the direction of a bond and hybridization of orbitals, the direction of a bond and the bond angle, the bond energy and polarity, and the bond energy and orbital hybridization.
9. Is the bond polar or non-polar in the molecules CO, CO_2, HBr, and Br_2? Defend your answer.
10. Why are some molecules non-polar as a whole although they have polar bonds?

3.3. Ionic Bond

The difference in the electronegativity of interacting atoms leads to the formation of a polar bond because of the displacement of the electron density of the molecular orbital toward the more electronegative atom. If the difference between the electronegativities of the atoms is very great, we can

speak about the complete transition of an electron pair to the more electronegative atom. In a simplified way, this consists in the transfer of an electron from one atom to another, for example in the formation of sodium chloride NaCl. The interaction of sodium and chlorine atoms in accordance with the ionic bond theory is attended by the transfer of an electron from sodium to chlorine. The neutral sodium atom loses an electron and transforms into a positively charged ion (cation), while the chlorine atom acquires an electron and transforms into a negatively charged ion (anion). The alkali metals are known to have only one *s* electron in their outer level. They have one more electron than atoms of the preceding noble gases. Since the alkali metals are characterized by a low ionization energy, it is the easiest for them to form cations. The alkaline-earth metals behave similarly.

The electron configurations of the outer shells of the halogens—elements of Subgroup VIIA—are the same, namely, s^2p^5. This means that a halogen lacks one electron to complete an eight-electron shell. Consequently, when an alkali metal combines with a halogen, the transfer of an electron can be depicted schematically as follows:

$$Na^0 - e^- \rightarrow Na^+$$

$$Cl^0 + e^- \rightarrow Cl^-$$

The process results in the formation of oppositely charged ions that then interact with each other owing to electrostatic attraction. A chemical bond based on the electrostatic interaction of ions is called an **ionic** one.

Sodium is characterized by the formation of the stable ion Na^+ having the electron structure of neon, i.e. the noble gas preceding it in the periodic table. In a chlorine ion, the structure of the outer shell corresponds to the configuration of the noble gas argon.

In the formation of an ionic bond, an ideally complete transfer of the electrons nevertheless fails to occur. This confirms the single nature of a covalent and ionic bond. Consequently, the latter is considered to be the limiting case of a polar bond.

It has been proved experimentally that when the most electropositive and electronegative elements react, a bond of mainly an ionic nature forms. All the stable monatomic anions have an electron structure corresponding to that of the noble gas in the relevant period, while the simplest cations have the electron structure of the noble gas of the preceding period (compare, for instance, Na^+ and Ne, K^+ and Ar). Unlike a covalent bond, an ionic one has neither a direction nor saturation. The forces of attraction between charges do not depend on the direction along which these charges approach one another (the absence of direction). Moreover, two unlike ions joined by forces of attraction do not lose their ability to interact with ions of the opposite sign. This illustrates the absence of saturation in an ionic

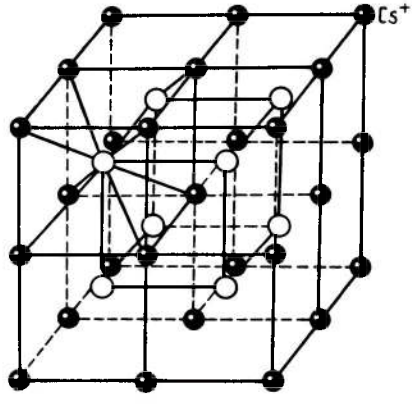


Fig. 17

Crystal lattice of cesium chloride

bond. A consequence of this feature of an ionic bond is the association of all the ions with the formation of an ionic crystal in which each ion is surrounded by ions of the opposite sign. The number of ions of the opposite sign retained by a given ion at the closest distance to it is called the **coordination number** of this ion. With a large size of the cation and a small radius of the anion (a ratio of $r_{cat} : r_{an} > 0.73$), eight anions (cations) are the closest to the cation (anion), and the coordination number is eight. The result is the formation of a crystal with a cubic structure—eight ions of the sign are at the apices of a cube at whose centre there is an ion of the opposite sign (of the type of CsCl, Fig. 17).

At a ratio of $r_{cat} : r_{an} < 0.73$, octahedral coordination of the ions occurs: each ion is surrounded by six counterions, i.e. the coordination number is six (of the type of NaCl, Fig. 18).

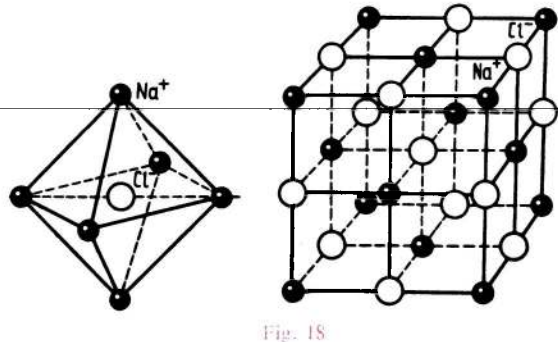


Fig. 18

Arrangement of six Na^+ ions around each Cl^- ion in the crystal lattice of sodium chloride

Ionic bonds are generally very strong, and since they extend throughout the entire volume of a crystal, solid crystalline substances of the ionic type are very refractory and have a high strength, but are brittle. They dissolve only in the most polar solvents such as water. The formulas generally ascribed to ionic substances [NaCl, CaF_2, $Al_2(SO_4)_3$, LiF, etc.] reflect only the composition, but tell nothing about the structure of a crystal and the arrangement of the ions in a substance.

Questions and Problems

1. Why does an ionic bond form in the halides of the alkali metals?
2. Explain the reasons and give examples of the similarity and difference of an ionic bond from a covalent one.
3. Is a covalent or ionic type of bond characteristic of the following compounds: NaI, SO_2, KF, CO_2?
4. Why is an ionic bond considered to be the limiting case of a covalent one?
5. Why do ions form when HCl dissolves in water, although the bond in the molecule is not ionic?
6. Why is the molecule Cl_2 non-polar, while ICl is polar?

3.4. Metallic Bond

There is an important feature in the atoms of metallic elements, namely, there are much less valence electrons than free orbitals. This provides conditions for the free migration of electrons among the orbitals of different atoms of the same metal. Owing to the low ionization energy, the atoms of a metal readily act on neighboring atoms of the same species and attract their electrons, which can immediately be pulled back, or migrate to a different neighboring atom. Hence, in a metal specimen, the electrons continuously move from atom to atom. The electrons, as it were, are simultaneously shared by all the atoms. This motion of the electrons is chaotic, and can become orderly only when a potential difference is set up between two points of the metal. This is exactly what explains the electrical conductance of metals.

Consequently, metals are characterized by a chemical bond that is based on the sharing of the valence electrons belonging not to two, but to practically all the atoms in a crystal. This bond is called a **metallic** one.

Unlike covalent and ionic compounds, in metals a comparatively small number of electrons simultaneously bind a multitude of atomic nuclei. This feature in the distribution of electrons is called **delocalization**. Therefore, the chemical bond in metals is delocalized.

This type of bond is typical of the solid and liquid states, while in the gaseous state atoms of metals are joined only by a covalent bond (Li_2, Cu_2, etc.).

Questions and Problems

1. In what features do a covalent, ionic, and metallic bonds differ? Why is a metallic bond singled out into a special type?
2. Why is the chemical bond in metals delocalized?
3. An "electron gas" can form in metals, but it cannot form in non-metals. Why?

3.5. Interaction between Molecules. Hydrogen Bond

The existence of substances in various states of aggregation indicates that interaction occurs between particles (atoms, ions, molecules) owing to forces of attraction. The latter were first described by the Dutch physicist J. van der Waals and were later named the van der Waals forces.

The most important and distinguishing feature of van der Waals forces is their universal nature because they act between all atoms and molecules with no exception.

Proceeding from the modern notions on the structure of an atom, we can substantiate the impossibility of the existence of the hypothetic molecule He_2, but this does not yet indicate that there is in general no interaction between helium atoms. Since helium and the other noble gases can be transferred into the liquid and even into the solid state, this already points to there being forces of attraction between atoms of the noble gases. The exceedingly low temperatures needed to liquefy the noble gases confirm that these forces are very insignificant.

There are several explanations of the nature of the van der Waals forces, the most important of which is electrostatic interaction. It is based on the fact that although atoms or molecules as a whole are electrically neutral, instantaneous electrical dipole moments constantly appear in them because of the orbital motion of the electrons. The interaction of the instantaneous and induced dipole moments is called **dispersion interaction.**

There are molecules with a constant electrical dipole moment. They can interact both with similar molecules and with non-polar ones, but are capable of polarization. This phenomenon is called **orientation interaction.**

If a polar and non-polar molecules come into contact, under the influence of the polar molecule the non-polar one is polarized and a dipole is induced in it. The induced dipole is attracted to the constant dipole of the polar molecule. Such interaction is called **induced.**

The considered types of interaction are varieties of electrostatic interaction.

The **hydrogen bond** is a variety of interaction between polar molecules. This bond forms between molecules of the HX type, where X stands for F, O, N, Cl, Br, I, or a group of atoms such as OH. The bond between the hydrogen and one of these atoms is characterized by a sufficient polarity

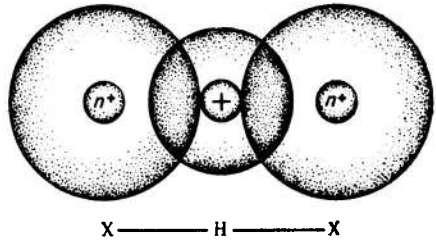
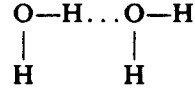


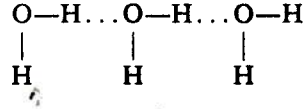
Fig. 19
Model of a hydrogen bond

because the bonding electron pair is displaced in the direction of the more electronegative atom. The hydrogen in this case is at the positive end of the dipole. Two and more of such dipoles interact with one another so that the nucleus of the hydrogen atom of one molecule (the positive end of the dipole) is attracted by the unshared electron pair of the second molecule (Fig. 19): X—H...X—H...X—H.

Let us consider the formation of a hydrogen bond in a molecule of water. Here a hydrogen atom is simultaneously attracted to the oxygen atom of the second molecule:



A hydrogen atom of the second molecule is attracted to the oxygen of the third molecule, and so on:



A hydrogen bond is designated by three dots.

The kind of hydrogen bond encountered in water is called an **intermolecular hydrogen bond.**

The formation of hydrogen bonds plays an important role in both chemical and biological systems. The existence of hydrogen bonds in water is exceedingly important for biological processes because the properties of water (its boiling and freezing points) are determined to a considerable extent by the presence of a system of bonds O—H...O—H. Owing to its hydrogen bonds, water has a boiling point that is much higher than ought to be expected in accordance with its molecular mass, while the melting point of ice exceeds that expected in accordance with its molecular mass by almost 200 K.

Questions and Problems

1. In what is a hydrogen bond similar to the other bonds and in what does it differ from them? Defend your answer.
2. A covalent bond forms by a dative mechanism with the aid of an unshared electron pair. Can we consider that a hydrogen bond forms by a dative mechanism?
3. Name the substances capable of forming a hydrogen bond.

SUMMARY

The most important branch of theoretical chemistry is that dealing with a chemical bond.

A covalent bond is formed by a shared electron pair whose cloud can be distributed in space differently relative to the nuclei of the atoms. If the cloud is symmetrical between the nuclei of the two atoms, such a bond is a non-polar covalent one. If the cloud is displaced from its symmetrical position in the direction of a more electronegative atom, the bond becomes polarized. Such a covalent bond is called a polar one.

Another variety of a chemical bond is an ionic one, which should be considered as the result of the complete transfer of an electron from one atom to another. Here the bond may be due to the forces of electrostatic attraction between particles of an opposite sign.

In metals, a metallic bond forms between atoms, its feature being that the valence electrons are free to move about among the multitude of atoms in a crystal (delocalization).

Chapter 4

CHEMICAL REACTIONS

OBJECTIVES

To classify chemical reactions on the basis of various features; to determine the rate of a chemical reaction and its mathematical expression; to derive the equation of the law of mass action; to define the principles of shifting of chemical equilibrium.

4.1. Heat Effect

A process involving the transformation of one set of substances into another set is called a **chemical reaction.**

The formation of new substances is a deep qualitative rearrangement associated with the destroying of some chemical bonds and the formation of others.

The destruction and formation of chemical bonds in a substance in the course of a reaction are attended by the expenditure of energy. The heat energy spent (or evolved) in the formation of a substance is called its **enthalpy (heat of formation)** and is designated by the letter H.

Assume that substances A and B react to form C and D:

$$A + B = C + D$$

Their enthalpies will be H_A, H_B, H_C, and H_D, respectively. There must always be a difference ΔH between the sum of the enthalpies of the products and the reactants. It is the **heat effect** of the chemical reaction.

If $H_C + H_D < H_A + H_B$, then ΔH is negative. If $H_C + H_D > H_A + H_B$, then ΔH is positive.

Reactions attended by the evolution of heat energy ($\Delta H < 0$) are called **exothermic**, while reactions attended by the absorption of heat energy ($\Delta H > 0$) are called **endothermic**. The heat effect of a reaction is always related to the reaction of an amount of substances (moles) indicated in the reaction equation. Chemical equations in which the heat effect of the reaction is indicated are called **thermochemical**.

For example, the thermochemical equation of the reaction of formation of nitrogen(II) oxide is:

$$N_2 + O_2 \rightarrow 2NO; \qquad \Delta H = 180.5 \text{ kJ}$$

It shows that the formation of two moles of nitrogen(II) oxide from nitrogen and oxygen is attended by the absorption of 180.5 kJ. This is an endothermic reaction.

The burning of hydrogen in oxygen is an exothermic reaction:

$$2H_2 + O_2 = 2H_2O; \qquad \Delta H = -571.6 \text{ kJ}$$

Thermochemical equations can be used to calculate the amount of heat evolved or absorbed in the course of a reaction.

Example. How much heat is evolved in the combustion of 24 g of graphite with the formation of CO_2? The thermochemical equation is:

$$C + O_2 = CO_2; \qquad \Delta H = -393.5 \text{ kJ}$$

Given:
$m(C) = 24$ g
$\Delta H = ?$

Solution. We see from the thermochemical equation that in the combustion of one mole of carbon 393.5 kJ of heat are evolved: $M(C) = 12$ g/mol.

In accordance with the initial conditions, we have

$$n(C) = \frac{24 \text{ g}}{12 \text{ g/mol}} = 2 \text{ mol}$$

Hence, the heat required for the combustion of two moles of graphite is $2 \times (-393.5) = -787$ kJ.

Questions and Problems

1. Compile the thermochemical equation if in the reaction of one mole of hydrogen with one mole of chlorine there is evolved 184.6 kJ of heat.

2. The thermochemical equation of the reaction of calcium carbonate decomposition is:

$$CaCO_3 = CaO + CO_2; \quad \Delta H = 157 \text{ kJ}$$

What amount of heat is spent on the decomposition of 325 g of $CaCO_3$?

3. Compile the thermochemical equation of the reaction if 3.77 kJ of heat is evolved when 2.1 g of iron react with sulphur.

4. Using the thermochemical equation given in problem 2, calculate the amount of heat required for the preparation of two moles of CaO.

4.2. Rate

If we mix two volumes of hydrogen with one volume of oxygen in a vessel, at standard temperature and pressure these gases can remain unchanged for an infinitely long time. If we heat the mixture, the formation of water will grow with elevation of the temperature. Finally, if we ignite the mixture, the reaction proceeds instantaneously. The reaction between ions in solutions mainly occurs very rapidly. The rate of any reaction can be determined on the basis of the changes that occur in a definite time interval. The rate of a reaction is usually determined by the change in the concentration of the reactants or products in unit time.

Let us consider a reaction proceeding at constant temperature and constant pressure:

$$A + B \rightarrow AB$$

Let the concentration of substance A at the instant t_0 be c_0. As the reaction proceeds, at the instant t_1 (where $t_1 > t_0$), the concentration of substance A diminishes as a result of formation of the product AB and is c_1 (where $c_1 < c_0$). During the time $t_1 - t_0$, the change in the concentration of substance A was $c_1 - c_0$, whence the rate of the reaction (i.e. the rate of the change in the concentration of substance A) is

$$J = \frac{c_1 - c_0}{t_1 - t_0} = \pm \frac{\Delta c_A}{\Delta t}$$

The concentration is expressed most frequently in mol/lit. The fraction is preceded by a minus sign when the decrease in the concentration of a reactant is being determined, and a plus sign if the growth in the concentration of a product is being determined for the same interval.

The rate of a reaction depends on many factors such as the nature and concentration of the reactants, the pressure (in reactions with the participation of gases), the temperature, the catalyst used, and the degree of comminution of the reactants (in reactions with the participation of solid substances).

The basic parameters that have to be taken into consideration in almost all processes are the concentration, temperature, pressure, and the action of catalysts. (The influence of the pressure on the reaction rate will be treated in Sec. 4.3 when considering examples of reactions with the participation of gases.)

Influence of Concentration on the Rate of a Reaction. Molecules can react only if they collide. Consequently, the more frequent these collisions are in a given time, the higher is the reaction rate. The probability of a collision between reacting particles grows with an increase in their concentration.

The influence of the concentration on the rate of a chemical reaction is expressed by the **law of mass action:**

at a constant temperature, the rate of a chemical reaction is directly proportional to the product of the reactant concentrations.

Since the rate of the reaction A + B → C is proportional to the product of the concentrations of substances A and B, i.e., using brackets to express the concentration, to the product of [A] and [B], we can write

$$J = k[A][B]$$

where k is the rate constant (proportionality factor) taking into account the difference between the units of the rate and concentration. The constant k indicates the number of collisions resulting in a reaction. If we assume that [A] = [B] = 1 mol/lit, then

$$J = k$$

Consequently, the rate constant is the rate of a reaction at reactant concentrations equal to unity.

If n molecules of substance A and m molecules of substance B enter into a reaction, i.e.

$$nA + mB \rightarrow qC$$

the coefficients n and m are exponents on the relevant concentrations, and now the law of mass action can be written as follows:

$$J = k[A]^n[B]^m$$

The equations showing how the rate of a reaction depends on the concentrations of the reactants are called **kinetic equations.**

The rate constant k depends on the nature of the reactants, the temperature, and on the presence of catalysts, but does not depend on the concentrations of the substances. The law of mass action is applicable only to gaseous and dissolved substances. If solids also participate in a reaction together with such substances and the concentration of the solids is constant, the rate of the reaction changes depending on the concentrations of

the gases or solutes. For instance, the rate of the reaction of sulphur combustion ($S + O_2 = SO_2$) is proportional only to the concentration of the oxygen, i.e. $J = k[O_2]$.

Influence of Temperature. The temperature dependence of the rate of a reaction is expressed in an approximate form by van't Hoff's rule according to which for every 10 kelvins of temperature elevation the rate of a reaction grows about two to four times. The number showing how many times the rate of a given reaction grows when the temperature is elevated by 10 K is known as the **temperature coefficient of a reaction.**

For a reaction to begin between reactants, it is first necessary to break or weaken the bonds between the atoms in them, i.e. to activate them. This requires the expenditure of the relevant energy called the **activation energy.**

The activation energy can be said to be a sort of energy barrier that separates the reactants from the products. The energy spent on activation of the molecules is evolved completely or partly in the formation of the products. If more energy is evolved than is needed for activation of the molecules, the reaction is exothermic, while if less energy is evolved, the reaction is endothermic.

Catalysis. In laboratory practice, the reaction of decomposition of potassium chlorate is often used to obtain oxygen:

$$2KClO_3(s) \xrightarrow{t} 2KCl(s) + 3O_2(g)$$

The process goes on very slowly even when the reactant is heated very strongly, but if a little MnO_2 is added prior to heating the $KClO_3$, the reaction rate grows substantially. After termination of the reaction, virtually all of the manganese(IV) oxide remains unchanged both qualitatively and quantitatively.

Substances that change the rate of a chemical reaction while remaining unchanged both qualitatively and quantitatively toward the end of the reaction are called catalysts.

A process conducted in the presence of a catalyst is called **catalysis,** while reactions in which the rate changes as a result of the introduction of catalysts into the reaction system are called **catalytic.**

Biochemical reactions in plants and animals are accelerated by biological catalysts called **enzymes.** They are either high-molecular-weight proteins or a combination of proteins with compounds of a non-protein nature. Each enzyme is characterized by a high selectivity with respect to a specific process. For example, the oxidation of sugar in an organism proceeds about 10^6 times more rapidly than at the same temperature in an aqueous solution under the influence of oxygen. Several enzymes take part in the complex chain of the biochemical processes involved in the oxidation of sugar in an organism, and each of them catalyzes a separate step.

Depending on whether a catalyst is in the same state of aggregation (in the same phase) as the reactants or is not, we distinguish homogeneous and heterogeneous catalysis.

In homogeneous catalysis, the catalyst and reactants are in the same phase. A very simple example of homogeneous catalysis is the oxidation of SO_2 to SO_3 in the presence of nitrogen(IV) oxide (the chamber process of sulphuric acid production):

$$SO_2(aq) + NO_2(aq) + H_2O = H_2SO_4 + NO$$

The formed NO is oxidized by the oxygen of the air to NO_2 and is recycled into the reaction:

$$2NO + O_2 = 2NO_2$$

Homogeneous catalysis in solutions is the most diversified. Numerous reactions are known that are catalyzed by acids and bases—what is known as acid-base catalysis (for example, the formation of ethers and esters in the presence of mineral acids, and the production of phenolformaldehyde resins).

In heterogeneous catalysis, the catalyst is in a different phase than the reactants. For example, in the contact method of producing sulphuric acid, SO_2 is oxidized by oxygen in the presence of a solid catalyst. The mechanism of heterogeneous catalysis is much more involved than that of homogeneous catalysis. One of the initial stages is the adsorption of the reactants of the surface of the catalyst with the subsequent formation of intermediates between the reactant molecules and the atoms (or ions) in the surface layer of the catalyst. Next the intermediates, which have a much lower activation energy than the reactants, readily react with one another. Hence, the essence of catalysis is lowering of the activation energy of the reactants.

Questions and Problems

1. What factors affect the rate of a chemical reaction? Explain their influence.
2. The homogeneous reaction $2NO + Cl_2 = 2NOCl$ has a simple mechanism. Which equation properly reflects the dependence of the rate of this reaction on the concentration of the reactants: (a) $J = k[NO]^2$; (b) $J = k[Cl_2]$; (c) $J = k[NO]\,[Cl_2]$; (d) $J = k[NO]^2[Cl_2]$? How will the rate of this (forward) reaction change if the concentration of the nitrogen(II) oxide is halved?
3. How many times will the rate (rate constant) of a chemical reaction grow when the temperature is increased by 40 K if the temperature coefficient of the reaction is two?
4. By how many kelvins must the temperature in a reaction mixture be lowered to reduce the rate of the reaction 27 times if the temperature coefficient of this reaction is three?
5. Find the temperature coefficient of a reaction if its rate increased 32 times when the temperature was elevated by 50 K.
6. Give examples of catalytic reactions.

4.3. Chemical Equilibrium

Reversible and Irreversible Reactions. We cannot succeed in conducting some chemical reactions to the end, i.e. achieve the complete conversion of the reactants. For example, the reaction of equimolar amounts of hydrogen and iodine proceeds at 350 °C until 80% of HI forms of the theoretically possible amount. The remaining 20% of H_2 and I_2 regardless of the duration of holding them at this temperature remain unchanged.

If HI is heated and kept at 350 °C, it decomposes into the initial H_2 and I_2, but the process occurs so that 10% of H_2 and 10% of I_2 form, while the remaining 80% of the HI does not decompose:

$$2HI = H_2 + I_2$$

Consequently, at 350 °C two processes go on, namely, a forward reaction in which H_2 and I_2 combine to form HI, and a reverse reaction in which the formed HI partly decomposes into the initial H_2 and I_2. The forward and reverse reactions characterize the state of chemical equilibrium.

Reactions proceeding simultaneously in two opposite directions are said to be **reversible.** When writing such reactions, the equality sign is replaced with oppositely directed arrows:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

Let us consider the reaction of magnesium with hydrogen chloride:

$$Mg + 2HCl = MgCl_2 + H_2\uparrow$$

This reaction yields magnesium chloride and hydrogen. If we try to conduct the reverse reaction, i.e. pass hydrogen through a solution of $MgCl_2$, metallic magnesium and HCl are not obtained. Hence, the reaction proceeds only in one direction and is therefore said to be **irreversible.** Such reactions include ones attended by the formation of weakly dissociated compounds, or reactions whose products are removed from the reaction medium.

In chemical equilibrium, the concentrations of the reactants and products remain unchanged. But chemical equilibrium should not be understood as something that is static and reminds one of equilibrium on a balance. It should be remembered that in equilibrium, both the forward and the reverse reactions proceed continuously, but at the same rate. The system as a whole is in motion, therefore this equilibrium is called dynamic.

Let us consider the kinetic conditions under which equilibrum can set in. With time, the rate of any reaction measured by the drop in the concentration of the reactants will diminish because the reaction of substances

is attended by a drop in their concentrations. But if a reaction is reversible, for example

$$CO + NO_2 \rightleftarrows CO_2 + NO$$

then the drop in the concentrations of the reactants and, consequently, the diminishing of the rate of the forward reaction will be attended by a growth in the rate of the reverse reaction because the concentration of the products—CO_2 and NO—grows:

for the forward reaction, $J_1 = k_1[NO_2][CO]$;
for the reverse reaction $J_2 = k_2[CO_2][NO]$.

As soon as the values of J_1 and J_2 are the same, dynamic equilibrium will set in in the system, and no further change in the concentrations of the reactants and products will occur. Hence, in a state of chemical equilibrium, we have $J_1 = J_2$, i.e. $k_1[NO_2][CO] = k_2[CO_2][NO]$. In the given equation, $[NO_2]$, [CO], [NO], and $[CO_2]$ are the equilibrium concentrations of the substances. Let us write the above equation in the form of a proportion:

$$\frac{k_1}{k_2} = \frac{[NO][CO_2]}{[NO_2][CO]}; \qquad \frac{k_1}{k_2} = K.$$

The quantity K is called the **chemical equilibrium constant.** It does not depend on the concentrations of the reactants and is constant for a given temperature. For any equilibrium system $mA + nB \rightleftarrows pC + qD$, the equilibrium constant is related to the equilibrium concentrations by the general formula:

$$K = \frac{[C]^p[D]^q}{[A]^m[B]^n}$$

This equation is a mathematical expression of the law of mass action that is obeyed by a system in a state of equilibrium. It shows that in reversible reactions equilibrium sets in when the ratio of the product of the equilibrium product concentrations to the product of the equilibrium reactant concentrations becomes equal to a constant quantity for the given reaction. Each concentration is included in the expression of the equilibrium constant raised to a power equal to the stoichiometric coefficient of the given substance in the reaction equation.

For heterogeneous reactions, the expression of the equilibrium constant, like the expression of the law of mass action for the rate of a chemical reaction, includes the concentrations of only the substances that are in the less condensed phase. For example:

$$CO_2(g) + C(s) \rightleftarrows 2CO(g); \qquad K = \frac{[CO]^2}{[CO_2]}$$

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g); \qquad K = [CO_2]$$

The value of K depends on the nature of the reactants and on the temperature, but does not depend on the catalyst. The presence of a catalyst in a system only cuts the time needed for equilibrium to set in.

The value of the equilibrium constant enables one to judge on how far a reaction proceeds.

When $K \geqslant 1$, equilibrium sets in when almost all the reactants have entered into the reaction, and equilibrium "shifts to the right".

When $K \leqslant 1$, only a small amount of the reactants are transformed into the products, and equilibrium shifts to the left.

Shift of Chemical Equilibrium. Le Chatelier's Principle. The equilibrium position (i.e. equality of the rates of the forward and reverse reactions and constancy of the concentrations of all the substances in the system) does not change as long as desired under constant external conditions (temperature, while if gaseous substances participate in the reaction, and pressure). When the temperature of a system changes, or the concentrations of the reagents change, the rates of the forward and reverse reactions always change differently. This causes the concentrations of the substances in the system to change, and the process continues until the rates of the forward and reverse reactions become equal under the new conditions. Equilibrium sets in again, but already at different concentrations than previously. The disturbance of equilibrium due to a change in one of the conditions of existence of the given system is called a **shift of chemical equilibrium.**

A change in the pressure makes equilibrium shift only when the amount of the gaseous substances (number of moles) before and after a reaction differs.

When chemical equilibrium shifts, it is important to know the direction in which the shift will occur when one of the conditions changes (the temperature, concentration, or pressure). The direction of a shift in equilibrium can be predicted qualitatively by using **Le Chatelier's principle:** *if a stress (a change in the temperature, concentration, or pressure) is applied to a system in equilibrium, the position of equilibrium of the system will shift in such a direction as to reduce the stress.*

Let us consider as an example the reaction of oxidation of sulphur(IV) oxide to sulphur(VI) oxide:

$$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g); \qquad \Delta H = -791.6\ \text{kJ}$$

The reaction of formation of SO_3 is attended by the evolution of heat, i.e. it is exothermic. The opposite process, i.e. the decomposition of SO_3 into the reactants, is endothermic. If the temperature is raised after equilibrium has set in, this stress will shift equilibrium in the direction counteracting this change, i.e. in the direction of the reaction with the absorption of heat. The decomposition of SO_3 is such a reaction.

When the temperature is raised, the endothermic process comes to the forefront in the system. When the temperature is lowered, the exothermic process begins to predominate. We can thus conclude that if the temperature of an equilibrium system is changed, elevation of the temperature shifts equilibrium in the direction of the endothermic process. Lowering of the temperature, conversely, shifts equilibrium in the direction of the exothermic process. The influence of the pressure is determined by the change in the volume occurring during a reaction. In the above example, the pressure of the system will lower as SO_3 forms because only two moles of it form from every two moles of SO_2 and one mole of oxygen.

Consequently, when the pressure is increased, equilibrium will shift in the direction of formation of a smaller amount (number of moles) of the gas, while a reduction in the pressure shifts equilibrium in the direction of formation of a larger amount (number of moles) of the gas. Hence, in the above equilibrium system, an increase in the pressure will shift equilibrium in the direction of formation of SO_3.

When the concentration of the components of an equilibrium system changes, the value of the equilibrium constant remains unchanged, although equilibrum shifts because here more favourable conditions are created for the proceeding of the forward or reverse reaction. An increase in the concentration of SO_2 or O_2 (or both simultaneously) will shift equilibrium in the direction of formation of SO_3 as the process reducing the concentration of SO_2 and O_2. If the SO_3 is withdrawn from the reaction mixture as it forms, equilibrium will also shift to the right. Hence, if an excess of one of the reactants is introduced into a reaction mixture, equilibrium will shift in the direction of product formation. A similar result can be obtained by removing the products from the system.

Questions and Problems

1. Why is chemical equilibrium called dynamic?
2. Write the expression of the equilibrium constant for the reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3; \qquad \Delta H = -791.6 \text{ kJ}$$

3. What conditions increase the product yield in the above reaction?
4. How will an increase in the pressure and temperature affect the shift of equilibrium in the system

$$2CO \rightleftarrows CO_2 + C; \qquad \Delta H < 0$$

5. In which direction will equilibrium of the following reversible reaction shift with an increase in (a) the concentration of the tin(II) chloride, and (b) the concentration of the tin(IV) chloride?

$$SnCl_2 + 2FeCl_3 \rightleftarrows SnCl_4 + 2FeCl_2$$

6. In which direction will equilibrium shift in the reaction

$$CO(g) + H_2O(v) \rightleftarrows CO_2(g) + H_2(g); \qquad \Delta H = 43 \text{ kJ}$$

(a) when the concentration of the water is lowered; (b) when the temperature is raised; and (c) when the pressure is reduced?

7. Why does a change in the pressure fail to shift equilibrium in the system:

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

8. Write the expression of the equilibrium constant for the process:

$$Fe(s) + H_2O(v) \rightleftarrows FeO(s) + H_2(g)$$

Will the state of equilibrium change when (a) the amount of iron is increased in the system; and (b) when the pressure is changed?

4.4. Classification

Chemical reactions can be classified on the basis of various features. The simplest classification is by the number of reactants and products.

A **combination (addition) reaction** is one in which two or more substances (either elements or compounds) react to form one product that is more complicated than the reactants:

$$\left.\begin{array}{l} SO_3 + H_2O = H_2SO_4 \\ S + O_2 = SO_2 \\ NH_3 + HCl = NH_4Cl \end{array}\right\} \quad A + B = AB$$

A **decomposition reaction** is one in which one compound decomposes to form two or more substances. The products can be either simple substances, elements, or compounds:

$$\left.\begin{array}{l} 2HgO = 2Hg + O_2 \\ 2KClO_3 = 2KCl + 3O_2 \\ CaCO_3 = CaO + CO_2 \end{array}\right\} \quad AB = A + B$$

A **replacement (substitution)** reaction is one in which atoms of one element replace atoms of another element in a compound, the products being two new substances—an element and a compound:

$$\left.\begin{array}{l} Fe + CuSO_4 = FeSO_4 + Cu \\ Zn + 2HCl = ZnCl_2 + H_2 \end{array}\right\} \quad X + AB = AX + B$$

An **exchange (metathesis or double displacement) reaction** is one in which the reacting compounds exchange their constituent parts (usually ions), as a result of which two compounds form two new compounds:

$$\left.\begin{array}{l} BaCl_2 + Na_2SO_4 = 2NaCl + BaSO_4\downarrow \\ AgNO_3 + HCl = HNO_3 + AgCl\downarrow \end{array}\right\} \quad AB + CX = AX + CB$$

With respect to their thermochemical indices, chemical reactions can

be divided into **exothermic** ones:

$$C + O_2 = CO_2; \qquad \Delta H < 0$$

and **endothermic** ones:

$$CaCO_3 = CaO + CO_2; \qquad \Delta H > 0$$
$$N_2 + O_2 \rightleftarrows 2NO; \qquad \Delta H > 0$$

With a view to the use of catalysis, we distinguish **catalytic** and **non-catalytic** reactions. The former include all processes going on with the participation of catalysts, for instance, the reaction:

$$2SO_2 + O_2 \overset{cat.}{\rightleftarrows} 2SO_3$$

Non-catalytic reactions include any reactions proceeding instantaneously in solutions, for example:

$$BaCl_2 + H_2SO_4 = 2HCl + BaSO_4\downarrow$$

With respect to reversibility, reactions are divided into **reversible** and **irreversible** ones, which have been treated on earlier pages.

Questions and Problems

1. Which of the following reactions can be related to combination, decomposition, replacement, and exchange ones:

(a) $AgNO_3 + HCl = AgCl + HNO_3$
(b) $CaO + CO_2 = CaCO_3$
(c) $2CuO + C = 2Cu + CO_2$
(d) $Zn + 2HCl = ZnCl_2 + H_2$
(e) $Cu + S = CuS$
(f) $HgS = Hg + S$
(g) $Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$

2. What types can the following reactions be related to (with respect to different features):

(a) $2H_2 + O_2 = 2H_2O$, $\Delta H < 0$
(b) $MgCO_3 = MgO + CO_2$, $\Delta H > 0$
(c) $N_2 + 3H_2 \overset{cat}{\rightleftarrows} 2NH_3$, $\Delta H < 0$
(d) $Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$, $\Delta H < 0$
(e) $2KClO_3 \overset{cat.}{\rightleftarrows} 2KCl + 3O_2$, $\Delta H > 0$
(f) $H_2 + I_2 \rightleftarrows 2HI$

SUMMARY

The concept of the rate of chemical reactions is the basic one in chemical kinetics. The rate of a reaction depends on many factors, but the most important of them are the nature of the reactants, the concentration, temperature, pressure, and the action of a catalyst. At a constant temperature,

the rate of a reaction is directly proportional to the concentration of the reactants. This quantitative relation is known as the law of mass action.

The temperature dependence of the reaction rate is expressed by van't Hoff's rule. If a process goes on only in one direction, it is called irreversible. Processes going on in two opposite directions are called reversible. When the rates of the forward and reverse reactions in a reversible process become equal, dynamic equilibrium sets in in the system. Chemical equilibrium shifts in accordance with Le Chatelier's principle.

The laws of chemical kinetics cover all types of reactions. Their classification is based on various criteria.

CHAPTER 5

SOLUTIONS. ELECTROLYTIC DISSOCIATION

OBJECTIVES

To characterize the concepts "solution" and "solubility"; to determine the concentration of solutions and convert one concentration into another one expressed differently proceeding from the volumes and densities; to explain the process of dissolution and the heat phenomena attending this process; to describe the laws relating the solubility, pressure, temperature, and nature of the solute; to characterize acids, bases, and salts from the standpoint of electrolytic dissociation; to explain the processes occurring when acids, bases, and salts dissolve in water; to calculate the concentrations of H^+ and OH^- ions from the given parameters and to use the results to determine the pH of solutions.

5.1. General

The term "solution" is generally used to describe homogeneous mixtures in which the components are uniformly distributed throughout the entire volume.

Solutions are homogeneous systems of a variable composition consisting of two or more components.

The component that predominates quantitatively and is in the same state of aggregation as the formed solution is called the **solvent**. The other substance or substances in the solution are called **solutes**.

In general, the properties of solutions, and first of all their stability,

depend on the size of the distributed particles. By this feature, we distinguish **suspensions, colloidal,** and **true solutions.**

The particles of suspensions usually have a size of 10^{-5} to 10^{-7} m. Suspensions are featured by their instability in time, namely, the suspended particles (dispersed phase) either settle or rise to the surface depending on the ratio of the densities.

If the solute has a particle size under 10^{-9} m, the system is stable and does not separate when left standing for a long time. Such solutions are called true (or molecular) solutions.

Colloidal solutions are intermediate between true solutions and suspensions. The particles of colloidal solutions accordingly have a size ranging from 10^{-7} to 10^{-9} m.

The main feature characterizing a solution is its homogeneity. In this respect, solutions remind one more of a chemical compound and differ from mechanical mixtures. On the other hand, solutions do not have a strictly definite composition. This feature distinguishes them from chemical compounds.

5.2. Quantitative Characteristic of Solutions

The composition of a solution can be expressed either qualitatively or quantitatively. Usually when appraising solutions qualitatively, concepts such as a dilute and a concentrated solution are used. Solutions with a relatively low solute content are called **dilute,** while those with a relatively high solute content are called **concentrated.** This qualitative appraisal is very conditional because these concepts have their limitations for solutions of various substances. For example, for sulphuric acid, a solution containing 98% of H_2SO_4 is considered to be concentrated, whereas for HCl this term implies a solution containing 38% of HCl. Other concepts are employed for a more accurate quantitative appraisal of solutions. The amount of solute contained in a definite amount of solution or solvent is called the **concentration.** The latter can be expressed in different ways. One of them is to relate the mass m_1 of the solute to the total mass m of the solution and express the result as a percentage. The latter is called the **per cent concentration by mass** and is designated by the symbol w, i.e. $w = (m_1/m) \times 100\%$.

Another way of expressing the concentration is to relate the amount of the solute (its number of moles n) to the total volume of the solution V. The result is called the **molarity** or **molar concentration** of the solute and is designated by c, i.e. $c = n/V$. Generally the volume of the solution is taken equal to one litre (one decimetre) and is expressed in mol/lit. (The symbol M is still to be found in many books on the subject to express

the molarity, e.g. 0.1 *M* HCl denotes a concentration of $c = 0.1$ mol/lit, but its use is not recommended at present.)

The concentration can also be expressed by the number of moles of solute dissolved in 1000 g of solvent (**the molal concentration** or **molality**), by the ratio of the number of moles of a substance to the total number of moles of all the substances in the solution (the mole fraction), and in other ways.

To prepare a solution (either by mixing the solute and solvent, or the solvent with another solution, etc.), calculations must be performed to know how much of each of the substances must be taken.

Example 1. A salt in an amount of 15 g was dissolved in 135 g of water. What is the per cent concentration by mass of the solution.

Given:
m_1(salt) = 15 g
$m_2(H_2O)$ = 135 g
w(salt) = ?

Solution.
m (solution) = 135 + 15 = 150 g

$$w = \frac{m_1}{m} \times 100\% = \frac{15}{150} \times 100\% = 10\%$$

Example 2. What masses of a salt and water are needed to prepare 500 g of an 18% solution?

Given:
m(solution) = 500 g
w = 18%
m_1(salt) = ?
$m_2(H_2O)$ = ?

Solution.
m_1(salt) = m(solution) × w = 500 × 0.18 = 90 g
$m_2(H_2O) = m - m_1 = 500 - 90 = 410$ g

Example 3. What is the per cent concentration by mass in an evaporated solution if 1200 g of a 20% solution was evaporated to 800 g?

Given:
m_1(solution) = 1200 g
w_1 = 20%
m_2(solution) = 800 g
w_2 = ?

Solution.
m_1(salt) = m_1(solution) × w = 1200 × 0.2 = 240 g. During evaporation, a part of the water was removed from the solution, but the same amount of salt remained.

We determine w_2:

$$w_2 = \frac{m_1(\text{salt})}{m_2(\text{solution})} \times 100\% = \frac{240}{800} \times 100 = 30\%$$

Example 4. To 500 g of a 20% glucose solution there were added 300 g of water. What is the per cent concentration by mass of the glucose in the solution after dilution?

Given:
m_1(solution) = 500 g
w_1 = 20%
$m(H_2O)$ = 300 g
w_2 = ?

Solution.
m(glucose) = $m_1 w$ = 500 × 0.2 = 100 g
When the solution is diluted, the mass of the glucose remains unchanged. We find the mass of the dilute solution m_2:

m_2(solution) = m_1(solution) + $m(H_2O)$ = 500 + 300 = 800 g. We determine w_2:

$$w_2 = \frac{m(\text{glucose})}{m_2(\text{solution})} \times 100\% = \frac{100}{800} \times 100\% = 12.5\%$$

Example 5. In 300 g of water there were dissolved 100 lit of NH_3 at STP. What is the per cent concentration by mass of the ammonia in the solution?

Given:
$m(H_2O) = 300$ g
$V(NH_3) = 100$ lit
$w = ?$

Solution.
We find the mass of the ammonia $m(NH_3)$:
$m(NH_3) = Mn(NH_3)$; $n(NH_3) = V(NH_3)/V_m$
$m(NH_3) = MV(NH_3)/V_m$

$M(NH_3) = 17$ g/mol and $V_m = 22.4$ lit/mol (at STP).
$m(NH_3) = 17 \times 100/22.4 = 75.89$ g

We find the mass of the solution:

$$m(\text{solution}) = m(H_2O) + m(NH_3) = 300 + 75.89 = 375.89 \text{ g}.$$

We find the per cent concentration by mass of the ammonia in the solution:

$$w = \frac{m(NH_3)}{m(\text{solution})} \times 100\% = \frac{75.89}{375.89} \times 100\% = 20.19\%$$

Example 6. What is the per cent concentration by mass of sulphuric acid in a solution after dilution if 50 ml of a 96% solution of H_2SO_4 with a density of 1.836 g/ml were diluted with 250 ml of water?

Given:
$V(\text{solution}) = 50$ ml
$w_1 = 96\%$
$\varrho_1(\text{solution}) = 1.836$ g/ml
$V(H_2O) = 250$ ml
$w_2 = ?$

Solution.
We determine the mass of the initial solution:
$m_1(\text{solution}) = V(\text{solution})\varrho_1(\text{solution}) = 50 \times 1.836 = 91.8$ g.
The content of the acid in it is
$m(H_2SO_4) = m_1(\text{solution})w_1 = 91.8 \times 0.96 = 88.128$ g of H_2SO_4

The density of water $\varrho(H_2O) = 1$, and its mass $m(H_2O) = 250 \times 1 = 250$ g. The mass of the solution after dilution is $m_2(\text{solution}) = m(H_2O) + m(H_2SO_4) = 250 + 91.8 = 341.8$ g

After dilution, the per cent concentration by mass of the sulphuric acid in the solution is:

$$w_2 = \frac{m(H_2SO_4)}{m_2(\text{solution})} \times 100\% = \frac{88.128}{341.8} \times 100\% = 25.78\%$$

Example 7. In 135.6 g of water there are dissolved 64.4 g of Glauber salt $Na_2SO_4 \cdot 10H_2O$. What is the per cent concentration by mass of the anhydrous salt in the solution?

Given:
$m(H_2O) = 135.6$ g
$m(Na_2SO_4 \cdot 10H_2O) = 64.4$ g
$w = ?$

Solution.
$m(\text{solution}) = m(H_2O) + m(Na_2SO_4 \times 10H_2O) =$
$= 135.6 + 64.4 = 200$ g.

We find the mass of the anhydrous sulphate in the crystallohydrate. Since one mole of $Na_2SO_4 \cdot 10H_2O$ contains one mole of Na_2SO_4, then $M(Na_2SO_4 \cdot 10H_2O) = 322$ g/mol, and $M(Na_2SO_4) = 142$ g/mol. Hence,

$$m(Na_2SO_4 \cdot 10H_2O) = nM = 1 \times 322 = 322 \text{ g}$$
$$m(Na_2SO_4) = 1 \times 142 = 142 \text{ g}$$

We compile a proportion:

322 g of $Na_2SO_4 \cdot 10H_2O$ contain 142 g of Na_2SO_4
64.4 g of $Na_2SO_4 \cdot 10H_2O$ contain m_1 g of Na_2SO_4

$$m_1 = \frac{142 \times 64.4}{322} = 28.4 \text{ g}$$

We find the per cent concentration by mass of the anhydrous salt in the solution:

$$w = \frac{m_1(Na_2SO_4)}{m(\text{solution})} \times 100\% = \frac{28.4}{200} \times 100\% = 14.2\%$$

Example 8. To determine the per cent concentration by mass in a potassium iodide solution, 100 ml of a gas mixture containing chlorine were passed through 200 g of the solution. As a result, 0.508 g of crystalline iodine separated. What was the per cent concentration by mass of the potassium iodide in the initial solution? What volume of chlorine was contained in the gas mixture?

Given:
m(solution) = 200 g
V(gas mixture) = 100 ml
$m(I_2)$ = 0.508 g

w(KI) = ?
$V(Cl_2)$ = ?

Solution.
We compile the equation of the reaction between the potassium iodide solution and the chlorine in the gas mixture:

$$\underset{2\text{ mol}}{2KI} + \underset{1\text{ mol}}{Cl_2} = 2KCl + \underset{1\text{ mol}}{I_2}$$

Knowing the mass of the separated iodine, we can use this equation to calculate the mass of the potassium iodide and the volume of the chlorine that entered into the reaction.

The potassium iodide and iodine by the reaction equation are in a molar ratio of 2:1. The molecular weight of iodine is $M(I_2) = 127 \times 2 = 254$ g/mol. According to the initial conditions,

$$n(I_2) = \frac{0.508}{254} \text{ mol}$$

Consequently,

$$n(KI) = \frac{0.508 \times 2}{254} \text{ mol}$$

$$M(KI) = 39 + 127 = 166 \text{ g/mol}$$

$$m(KI) = M(KI)n(KI) = 166 \times \frac{0.508 \times 2}{254} = 0.664 \text{ g}$$

We calculate w(KI) in the initial solution:

$$w(KI) = \frac{0.664}{200} \times 100\% = 0.332\%$$

We use the reaction equation to find the volume of chlorine, whose molar ratio to the iodine is 1:1 by this equation. The number of moles of the iodine is $n(I_2) = 0.508/254$ mol. Hence, the amount of chlorine is the same. Its volume is $V = V_m n$, where $V_m = 22.4$ lit/mol. Hence, $V(Cl_2) = 22.4 \times (0.508/254) = 0.0448$ lit = 44.8 ml.

Example 9. Determine the molar concentration (mol/lit) of a solution containing 5.6 g of potassium hydroxide in 50 ml.

Given:
V(solution) = 50 ml
m(KOH) = 5.6 g

c(mol/lit) = ?

Solution.
The molar concentration of a solution is expressed by the ratio of the amount of the solute to the volume of the solution in litres:

$$c = n/V$$

$n(KOH) = \frac{m}{M}$; M(KOH) = 56 g/mol, whence n(KOH) = 5.6/56 = 0.1 mol. The volume of the solution is V = 50 ml = 0.05 lit. Consequently, c = 0.1/0.05 = 2 mol/lit.

Example 10. The density of a 35% solution of sulphuric acid is 1.260 g/cm^3. Find the concentration of this solution in mol/lit.

Given:
$w = 35\%$
$\varrho = 1.260$ g/mol
c (mol/lit) = ?

Solution.
m(solution)$V\varrho$. We conditionally assume the volume to equal 1 lit or 1000 ml. Hence, m(solution) = 1000 × × 1.260 = 1260 g; $m(H_2SO_4) = m$(solution)w = 1260 × × 0.35 = 441 g.

We determine the concentration of the given solution (in mol/lit) by the formula $c = n/V$; for this purpose, we must first find the number of moles of H_2SO_4 by the expression $n = m/M$. Since the molecular weight of H_2SO_4 is M = 98 g/mol and m = 441, we have $n = 441/98 = 4.5$. The volume V = 1 lit, and $c = 4.5/1 = 4.5$ mol/lit.

Questions and Problems

1. Explain the expression "a 3% solution".
2. What is meant by "c = 3 mol/lit"?
3. "A solution with a 5% concentration". Why is this statement incorrect? What is the correct way to state this?
4. Determine the per cent concentration by mass of a sodium hydroxide solution if 30 g of the solution contain 2 g of NaOH.
5. It is necessary to prepare 350 g of a 60% solution of sugar in water. What masses of the substances are needed for this purpose?
6. What mass of a 25% solution can be prepared from 40 g of potassium nitrate? How much water is required for this?
7. The density of a 32% nitric acid solution is 1.198 g/cm^3. Express the concentration of the solution in mol/lit.
8. To 200 g of a 10% solution there were added 50 g of water. What was the per cent concentration by mass of the solute after dilution?
9. A mixture was prepared from 20 g of a 5% and 10 g of a 3% solutions of the same substance. What was the per cent concentration by mass of the substance in the resultant solution?
10[a]. What amount of HCl is contained in 2.5 lit of its solution with a concentration of c = 3 mol/lit?
11[a]. How many grammes of silver nitrate and water must be taken to prepare 175 g of a 5% solution?
12[a]. To 120 g of a 28% salt solution there were added 216 ml of water. What is the per cent concentration by mass in the resulting solution?
13[a]. What must the per cent concentration by mass of KNO_3 in a solution be for the salt to water ratio to be 1 mol:15 mol?
14[a]. In 5 lit of water there are dissolved 250 g of $BaCl_2 \times 2H_2O$. What is the per cent concentration by mass of the anhydrous salt in the solution?
15[a]. The density of a 14.7% solution of KOH is 1.135 g/cm^3. What is the concentration of this solution in mol/lit.
16[a]. What is the per cent concentration by mass of a solution obtained by dissolving 33.6 lit of HCl in 100 ml of water?
17[a]. One volume of a 96% solution of sulphuric acid (with a density of 1.836 g/cm^3) was mixed with 10 volumes of water. What is the per cent concentration by mass of the sulphuric acid in the solution?
18[a]. The evaporation of 200 g of a salt solution yielded 30 g of a dry residue. What was the per cent concentration by mass of the solute in the solution?

5.3. Solubility of Substances

Dissolution is a spontaneous process. The transition of a substance into a solution is attended by the gradual increase of the solution's concentration. But the reverse process also occurs—the separation of a substance from a solution (crystallization). Initially dissolution predominates, but with time the rates of these processes become equal and dynamic equilibrium sets in—the concentration of the solute remains constant. Such a state can continue for an indefinitely long time if the conditions under which the solution formed (for example, the pressure and temperature) are not changed. A solution in which such equilibrium is achieved is said to be **saturated.** Hence, **the solubility of a substance is defined as its ability to dissolve in a given solvent.**

The solubility is measured by the concentration of a solution that is saturated at the given temperature. The calculations are most often performed with respect to 100 g of the solvent. For example, at 18 °C, 35.86 g of sodium chloride dissolve in 100 g of water. This signifies that the solubility of NaCl at the indicated temperature is 35.86. This quantity is called the **solubility coefficient.**

As regards their solubility, solids are conditionally divided into readily soluble, sparingly soluble, and practically insoluble. If over 10 g of a substance dissolve in 100 g of water at 20 °C, the substance is said to be readily soluble. If 0.01-1 g dissolves under the same conditions, the substance is said to be sparingly soluble. If less than 0.01 g of a substance passes into a solution under the same conditions, it is said to be practically insoluble. This division is conditional, and there are no absolutely insoluble substances in nature.

The solubility of most solids diminishes with lowering of the temperature, therefore when saturated solutions are cooled, a part of the solute separates in the crystalline form. The explanation is that the same substance has a different solubility at different temperatures. The process attended by the separation of the solute when a hot saturated solution is cooled is called **crystallization** (or **freezing**). If a hot saturated solution is cooled slowly, crystallization may fail to occur, although a solution forms where the content of the solute is considerably higher than what is needed to obtain a saturated solution at the given temperature. Such solutions are called **supersaturated.** If a minute crystal of the solute is introduced into a supersaturated solution (a "seed"), crystallization begins on the faces of the introduced crystal (the centre of crystallization), and part of the solute separates in the form of crystals. The solution transforms from a supersaturated into a saturated one. Quite often, crystallization from a supersaturated solution begins after a light jolt of the solution. The same effect is

observed if a glass rod is introduced into the solution and rubbed against the vessel walls.

Crystallization from solutions and recrystallization are widely used to purify substances dissolved in water or in other solvents.

The solubility depends not only on the temperature, but also on the nature of the solvent and solute. The relation between the temperature and solubility of solids is depicted graphically by the relevant solubility curves, as shown in Fig. 20. The example of sodium sulphate (Fig. 21) shows that with elevation of the temperature the solubility of this salt rapidly grows, increasing from 5 g per 100 g of water at 0 °C to 55 g at 32.4 °C. Above this temperature, the solubility drops from 55 g at 32.4 °C to 42 g at 100 °C. This behaviour is explained by the fact that at 32.4 °C the hydrate $Na_2SO_4 \times 10H_2O$ is in equilibrium with anhydrous sodium sulphate.

Gases can dissolve in liquids in two ways: either by distribution of the gas molecules in the medium of the solvent (e.g., the dissolving of O_2, N_2, and CH_4 in water), or as a result of chemical reaction between them (the dissolving of NH_3 in water). As saturation is reached, the gas molecules can gradually evolve from the solution. If the rate of evolution of the gas from the liquid equals that of dissolution, then at constant pressure and temperature dynamic equilibrium sets in, and the liquid is saturated with the gas.

The solubility of gases in water diminishes in the presence of polar or ionic substances. This is explained by the fact that they bind part of the

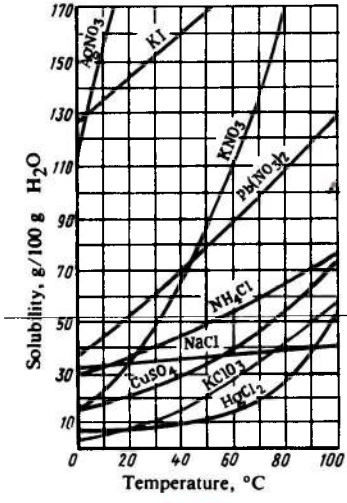


Fig. 20
Temperature dependence of the solubility of selected salts in water

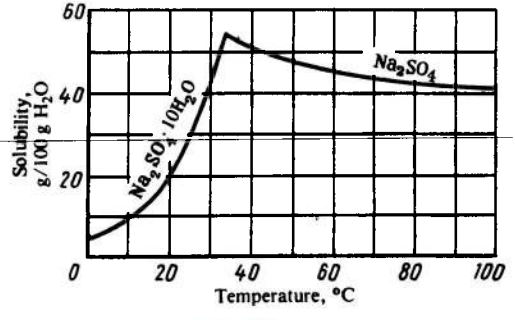


Fig. 21
Temperature dependence of the solubility of sodium sulphate in water

solvent molecules, and a smaller amount of the unbound solvent remains for dissolving the gas. Ionic (or polar) substances have much stronger bonds with solvent molecules than gases do. Substances dissolve readily in solvents related to them from the viewpoint of the chemical bond (the rule of like in like). The meaning of this rule from the viewpoints of our modern notions on the structure of molecules consists in that if the solvent molecules are not polar or are only slightly polar, the solvent will dissolve substances with non-polar or slightly polar molecules well, substances with a greater polarity worse, and will virtually not dissolve substances with an ionic type of structure. This rule can be illustrated using the example of the dissolving of one liquid in another. For instance, methanol or ethanol, being polar substances, mix readily with water in any proportions. Molecules of the alcohols are known to be associated at the expense of hydrogen bonds; this is also typical of liquid water. When these substances are mixed, the polar molecules of H_2O react with the molecules, say, of C_2H_5OH, and hydrogen bonds form between them. This causes greater disorder of the ethanol and water molecules, which is one of the important criteria of the miscibility of liquids.

Consequently, substances with the same type of interaction between the molecules are miscible (mutually soluble).

The solubility of a liquid in a liquid usually grows with an increasing temperature and does not virtually depend on the pressure. In liquid-liquid systems, when the solubility of the first liquid in the second one or of the second liquid in the first one is limited, separation is observed.

Since the solubility generally grows with elevation of the temperature, then at a certain temperature complete miscibility occurs. This temperature is called the **critical solution temperature,** and above it no separation occurs.

Questions and Problems

1[a]. When completely evaporating 300 g of an aqueous solution of KNO_3 saturated at 60 °C, there were obtained 157.01 g of a dry residue. What is the solubility of the salt at the indicated temperature?

2[a]. At 60 °C, 200 g of a saturated solution contain 36.57 g of anhydrous $CuSO_4$. What is the solubility of blue vitriol $CuSO_4 \cdot 5H_2O$ at this temperature?

3. Using solubility curves (see Fig. 20), find the solubility of potassium chlorate $KClO_3$ at 10 and 50 °C and the solubility of potassium nitrate KNO_3 at 30, 50, and 70 °C.

5.4. The Dissolution Process. Thermal Phenomena in Dissolution

Dissolution is an involved physicochemical phenomenon and depending on the nature of the solvent and solute, either a physical or a chemical process may predominate. A physical process generally precedes a chemical

one. D. Mendeleev when substantiating the theory of solutions was the first to advance the idea that chemical compounds exist in them. This idea formed the foundation of the chemical theory of solutions.

Usually the dissolution of one substance in another can follow one or several mechanisms. For example, the reaction of a metal with an acid is chemical dissolution occurring as a result of a specific chemical transformation:

$$Mg + 2HCl = MgCl_2 + H_2$$

Chemical dissolution is a process yielding the relevant solution of the target product. For instance, one can easily calculate the masses of P_2O_5 and H_2O needed to obtain a solution of H_3PO_4 of a definite concentration:

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

Solutions of the molecular or ionic type form as a result of such processes. In non-chemical dissolution, the process of interaction between the molecules of the solute and those of the solvent is called **solvation,** and the interaction products are called **solvates.** If water is used as the solvent, the process is called **hydration,** and the products are **hydrates.** Solvates can form in different ways depending on the nature of the solvent and solute. For example, if substances with an ionic structure are being dissolved, the solvent molecules are retained at the formed ion by the electrostatic forces of interaction. When some salts of doubly and triply charged ions such as Cu^{2+}, Al^{3+}, and Ni^{3+} dissolve, solvated ions form, namely: $[Cu(H_2O)_4]^{2+}$; $[Ni(H_2O)_6]^{3+}$, and $[Al(H_2O)_6]^{3+}$. The number of water molecules associated with an ion of the solute depends on its structure and size. When the radius of the ion is smaller, less water molecules can be associated with it. Large ions such as Na^+, K^+, and Cs^+ can be solvated by a various number of solvent molecules depending on the concentration of the solution.

The solvates (hydrates) are often so strong that they can be separated from the solution in the crystalline state. Such crystals containing solvent molecules in the bound form are called crystalline solvates (if the solvent is water, they are called crystalline hydrates or crystallohydrates). Examples of crystallohydrates are $CuSO_4 \cdot 5H_2O$, $Na_2SO_4 \cdot 10H_2O$, and $BaCl_2 \cdot 2H_2O$.

When the bond energy between the solvated particles and the solvent molecules becomes greater than the bond energy between the particles in a solid crystal, the entire crystal gradually disintegrates.

Consequently, when substances dissolve, the bonds between the ions, atoms, or molecules break, which is associated with the expenditure of energy. Simultaneously, the solute particles react with the solvent, which is attended by the evolution of energy. The overall energy effect depends on

the ratio of the evolved and absorbed energy. If the energy spent on breaking the bonds in the initial substance exceeds that evolved in the formation of a solvate, the temperature of the solution lowers, and if the opposite occurs, the temperature of the solution rises. The heat energy evolved or absorbed in the dissolution of substances is called the **heat of solution.**

Dissolution can thus be considered as two consecutive processes:

(1) breaking of the bonds in the initial substance (an endothermic process):

$$AB \rightarrow A + B$$

(2) solvation (hydration) of the particles A and B with the formation of solvates (hydrates) and the evolution of heat energy (an exothermic process):

$$A + nH_2O \rightarrow A \cdot nH_2O$$
$$B + nH_2O \rightarrow B \cdot nH_2O$$

The heat effect of dissolution is determined by the nature of the solvent and solute. For example, when concentrated sulphuric acid is mixed with water, so much heat is evolved that the solution may boil. Conversely, the dissolution of calcium chloride or ammonium nitrate is attended by great cooling.

Therefore, the dissolution of sulphuric acid is an exothermic process and $\Delta H < 0$; for calcium chloride $\Delta H > 0$ because the temperature drops when it is dissolved.

Questions and Problems

1. When ammonium nitrate is dissolved in water, the temperature of the solution drops below 0 °C, whereas when sodium hydroxide is dissolved, the temperature grows. Explain these phenomena.

2. Calculate the content of crystallization water in the following crystallohydrates in per cent: $CuSO_4 \cdot 5H_2O$, $Na_2SO_4 \cdot 10H_2O$, and $CaCl_2 \cdot 6H_2O$.

5.5. Electrolytes. Dissociation

A typical feature of aqueous solutions of salts, acids, and bases is their electrical conductance. At the same time, distilled water conducts an electric current very poorly, while dry crystalline salts or alkalies cannot conduct a current at all.

When studying the properties of solutions of salts, acids, and bases, S. Arrhenius concluded that the water molecules cause substances in a solution to **ionize.**

Substances whose aqueous solutions conduct electricity are called electrolytes.

Electrolytes include compounds whose molecules have a polar or ionic bond.

Substances whose aqueous solutions do not conduct an electric current are called non-electrolytes.

The process of decomposition of an electrolyte into ions in an aqueous solution is called electrolytic dissociation.

The mechanism of electrolytic dissociation was explained later in connection with the development of the theory of the chemical bond and chemical equilibrium. The decomposition of an electrolyte into ions in a solution occurs owing to complicated physicochemical interaction of the molecules with the polar molecules of water. If sodium chloride crystals are put in water, the polar molecules of the water acquire an ordered directed position relative to the ions in the crystal lattice of the salt. This interaction and the thermal motion of the water molecules cause the sodium chloride to decompose into ions:

$$NaCl \rightleftarrows Na^+ + Cl^-$$

In this case, the water molecules interact with the ions in the crystal lattice of the salt, as a result of which the hydrated ions pass into the solution (Fig. 22).

How great the role of the solvent is for dissociation can be seen from the behaviour of hydrogen chloride in water and, for instance, in benzene. A solution of HCl in benzene does not conduct electricity, hence ions are absent in the given solution, i.e. no dissociation occurs. An aqueous solu-

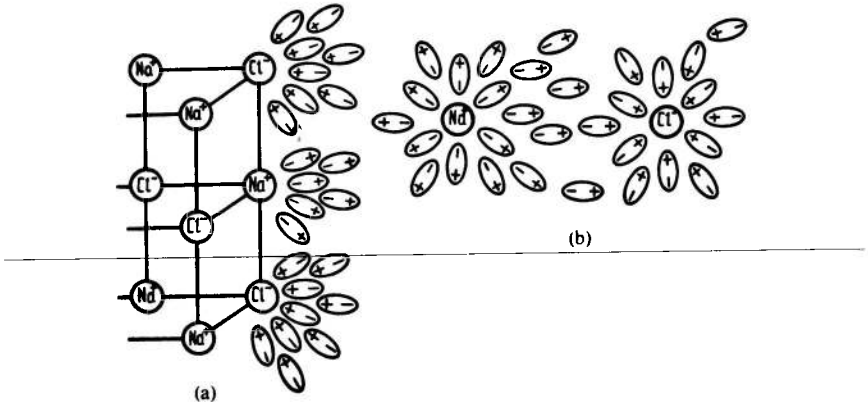


Fig. 22

Decomposition of sodium chloride crystals into separate ions under the influence of water dipoles:

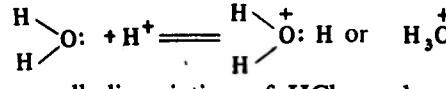
a—detachment of separate ions; *b*—hydrated sodium and chloride ions in the solution

tion of hydrogen chloride, on the other hand, contains H^+ and Cl^- ions, although gaseous HCl is a molecule with a covalent-polar bond.

The water dipoles cause the polar bond in HCl to become polarized still more, and finally ionization and dissociation of the HCl molecule take place:

$$HCl \rightleftarrows H^+ + Cl^-$$

Further, the hydrogen ion H^+ attaches itself to the oxygen atom in an H_2O molecule by a donor-acceptor mechanism. The pair of electrons for forming the bond is supplied by the oxygen atom. This can be depicted as follows:



Consequently, the overall dissociation of HCl can be described by the equation

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$

The formed H_3O^+ ion is called **hydroxonium.**

The consideration of the mechanism of electrolytic dissociation results in a number of important conclusions.

An electrolyte decomposes into ions only under the influence of a solvent having polar molecules. Only substances with polar molecules or ionic compounds are subjected to the action of water dipoles. Substances with a non-polar bond (Cl_2, H_2), and also with non-polar molecules (saccharose, glycerol, benzene, etc.) do not dissociate into ions and are therefore called non-electrolytes.

The dissociation of an electrolyte produces ions with unlike charges, namely positive (cations) and negative (anions) ones. The total charges of both species of ions are equal in magnitude, therefore an electrolyte solution is always electrically neutral.

If the concentration of an electrolyte is constant, then the content of ions in the solution does not change with time. The explanation is that ionization is attended by the reverse process—the formation of undissociated molecules from the ions. Hence, electrolytic dissociation is a reversible process.

Substances may also dissociate into ions in melts when heated (thermal dissociation). *But an electric current is never a cause of dissociation.*

Questions and Problems

1. Prove that electrolytic dissociation is a reversible process.
2. It is general knowledge that distilled water, although very poorly, nevertheless conducts an electric current, whereas crystalline table salt does not conduct one at all. What is the cause of these phenomena?
3. What is the relation between the type of chemical bond and electrolytic dissociation?

5.6. Degree of Dissociation. Factors Affecting It

The behaviour of aqueous electrolyte solutions in chemical reactions depends substantially on how completely the electrolytes decompose into ions. Of a major importance for a quantitative appraisal of dissociation are the degree of dissociation and the dissociation constant.

The **degree of dissociation** α is the ratio of the number of molecules n decomposing into ions to the initial number of molecules N of the solute:

$$\alpha = \frac{n}{N}$$

The degree of dissociation is sometimes expressed as a percentage:

$$\alpha = \frac{n}{N} \times 100\%$$

The degree of dissociation of electrolytes depends on the concentration of their solutions. With lowering of the concentration, the interaction of ions in a solution leading to the formation of molecules diminishes, and therefore the degree of dissociation grows. In accordance with their degree of dissociation, electrolytes are customarily divided into strong, weak, and moderate ones. Strong electrolytes have a degree of dissociation α over 30%, and weak ones—under 3%. Moderate electrolytes are inbetween, i.e. α ranges from 3 to 30%*.

Strong electrolytes in aqueous solutions include almost all the salts, most inorganic acids (HNO_3, HCl, H_2SO_4, $HClO_4$, etc.) and also the hydroxides of the alkali and alkaline-earth metals. The moderate electrolytes include H_2SO_3 and H_3PO_4. Compounds such as H_2S, HCN, H_2SiO_3, H_3BO_3, $Cu(OH)_2$, and $Cr(OH)_3$ are weak electrolytes.

The division of electrolytes into weak, moderate, and strong ones is conditional because the degree of dissociation depends on the nature of the electrolyte and solvent, and on the concentration and temperature of the solution. Aqueous solutions of various salts, acids, and bases of the same concentration dissociate to a different degree into ions. The degree of dissociation is appreciably affected by the presence of like ions in a solution. For instance, if a solution contains $CuCl_2$, then equilibrium of the system

$$CuCl_2 \rightleftarrows Cu^{2+} + 2Cl^-$$

can be shifted to the left by increasing the concentration of the Cu^{2+} or Cl^- ions. This is done by adding an electrolyte containing one of these ions to the solution. If a solution of HCl is added to one of $CuCl_2$, then owing to dissociation of the hydrogen chloride the concentration of the Cl^- ions in the solution will grow, and by Le Chatelier's principle equilibri-

* These values of α are given for a concentration of 0.1 mol/lit.

um will shift to the left, i.e. in the direction of diminishing the concentration of the Cl^- ions. The concentration of the undissociated $CuCl_2$ molecules will therefore grow.

The **dissociation constant** is the equilibrium constant (see Sec. 4.3) corresponding to the dissociation of a weak electrolyte.

Questions and Problems

1. Why do various electrolytes decompose into ions differently in a solution?
2. What facts confirm the reversibility of electrolytic dissociation?

5.7. Ionic Reactions

The reactions between electrolytes in solutions are reactions between the ions formed when the electrolytes dissociate. Such reactions are called **ionic.**

Let us consider the behaviour of two electrolytes in a solution. Assume that a solution contains NaCl and K_2SO_4. To reveal how these compounds react in aqueous solutions and what products form, we shall first consider the dissociation of these substances:

$$NaCl \rightleftarrows Na^+ + Cl^- \text{ and } K_2SO_4 \rightleftarrows 2K^+ + SO_4^{2-}$$

Both NaCl and K_2SO_4 dissolve well in water and are strong electrolytes. The ions in the solution can react in various combinations, namely, Na^+ with SO_4^{2-}, Na^+ with Cl^-, K^+ with Cl^- and K^+ with SO_4^{2-}. The possibility of forming each of the four substances—KCl, K_2SO_4, Na_2SO_4, and NaCl is equally probable, therefore when solutions of sodium chloride and potassium sulphate are mixed, no reaction occurs, i.e. an equilibrium system forms simultaneously containing all the ions.

Electrolytes can also react differently when weakly dissociating compounds form. For example, the reaction of sodium sulphate (a strong electrolyte) with barium chloride (a strong electrolyte) leads to the formation of two substances, namely, sodium chloride (a strong electrolyte) and barium sulphate (an undissociated compound) that precipitates:

$$Na_2SO_4 + BaCl_2 = 2NaCl + BaSO_4\downarrow$$

or in the ionic form:

$$2Na^+ + SO_4^{2-} + Ba^{2+} + 2Cl^- = BaSO_4\downarrow + 2Na^+ + 2Cl^-$$

The net ionic equation, which is exactly what shows the reaction of the ions and excludes all the "spectators", is:

$$Ba^{2+} + SO_4^{2-} = BaSO_4$$

This reaction is irreversible because the formation of the undissociated compound is attended by lowering of the concentration of the ions Ba^{2+} and SO_4^{2-}.

The above examples show that in ion-exchange processes, the reactions between the ions proceed in the direction of binding of the ions. A decrease in the concentration of certain species of ions in a solution causing equilibrium to shift occurs not only when a poorly dissociating compound forms, but also when volatile compounds form:

$$NH_4Cl + NaOH = NaCl + NH_3\uparrow + H_2O$$

$$NH_4^+ + OH^- = NH_3\uparrow + H_2O$$

Consequently, ionic reactions attended by the formation of precipitates (sparingly soluble substances), gases (volatile substances), or weak electrolytes (poorly dissociating compounds) proceed to the end. When compiling equations of ionic reactions, the substances that are insoluble in water, and also those that do not dissociate or dissociate weakly, are written in the molecular form, while all the remaining substances are written in the ionic form. For example,

$$Ag^+ + NO_3^- + K^+ + Cl^- = K^+ + NO_3^- + AgCl\downarrow$$

The reactants $AgNO_3$ and KCl, and also one of the products, i.e. KNO_3, are dissociated into ions because they are strong electrolytes. Only the ions Ag^+ and Cl^- react chemically to form the non-dissociating compound AgCl. The ions K^+ and NO_3^- remain in the solution and therefore do not affect the proceeding of the reaction. We exclude them and obtain the net ionic equation:

$$Ag^+ + Cl^- = AgCl\downarrow$$

Questions and Problems

Write the equations of the following reactions in the ionic and net ionic forms:

(a) $H_2SO_4 + Na_2CO_3 = Na_2SO_4 + CO_2\uparrow + H_2O$

(b) $FeSO_4 + Ba(NO_3)_2 = BaSO_4\downarrow + Fe(NO_3)_2$

(c) $CuCl_2 + 2AgNO_3 = 2AgCl\downarrow + Cu(NO_3)_2$

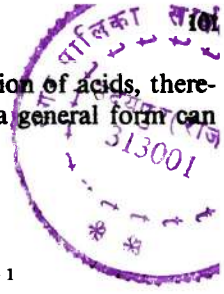
(d) $NaOH + HCl = NaCl + H_2O$

5.8. Acids and Bases

The concepts of an acid and base describe two classes of compounds whose properties are diametrically opposite. According to Arrhenius,

an acid is an electrolyte that yields hydrogen ions when it dissociates in water:

$$HCl \rightleftarrows H^+ + Cl^-$$



This presentation still underlies the chemical classification of acids, therefore from this standpoint the dissociation of acids in a general form can be written as

$$HA \rightleftarrows H^+ + A^-$$

or

$$HA + nH_2O \rightleftarrows H_3O^+ + A^-(H_2O)_{n-1}$$

i.e. acids are a source of H^+ ions.

The properties of acids (reaction with metals, basic oxides, bases; the ability to change the colour of indicators, and, finally, an acid taste) are due to the presence of H^+ ions. Polybasic acids dissociate in steps:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \text{ (1st step)}$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-} \text{ (2nd step)}$$
$$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-} \text{ (3rd step)}$$

The subsequent detachment of an H^+ ion from the acid residue $H_2PO_4^-$ formed in the first step occurs much more difficultly because of the presence of a negative charge on the anion. For this reason, the second stage of dissociation proceeds much more difficultly than the first one. The last, third proton should be detached from the HPO_4^{2-} anion (third stage), which has a still greater dispersion of the negative charge than $H_2PO_4^-$. This is why the third stage goes on by only 0.001%.

Bases are characterized by the metal atoms in them being bound to OH groups. The structural feature manifests itself in the form of general properties such as electrical conductance in aqueous solutions, the ability to react with acids (neutralization reactions) and change the colour of indicators. Since bases neutralize acids (the properties of acids are determined by the hydrogen ion), their solutions should contain ions that can bind hydrogen ions with the formation of water. These can only be OH^- ions:

$$OH^-(aq.) + H^+(aq.) \rightleftarrows H_2O$$

It follows that bases dissociate in aqueous solutions with the formation of OH^- ions:

$$NaOH \rightleftarrows Na^+ + OH^-$$
$$Ca(OH)_2 \rightleftarrows Ca^{2+} + 2OH^-$$

i.e. bases are sources of OH^- (hydroxyl) ions. Hence,

bases are electrolytes that in dissociation yield hydroxyl ions.

The M—OH bond is stronger when the charge of the metal ion M is greater and its radius is smaller. This is why the strength of bases formed by elements within one period decreases with an increase in the atomic number. If the same element forms several bases [CuOH and $Cu(OH)_2$,

$Fe(OH)_2$ and $Fe(OH)_3$], the value of the degree of dissociation α diminishes with a growth in the oxidation state of the metal. Therefore, the degree of basic dissociation of $Fe(OH)_2$ is greater than that of $Fe(OH)_3$.

The dissociation of bases containing two or more OH groups occurs in steps:

$$Zn(OH)_2 \rightleftarrows (ZnOH)^+ + OH^-$$
$$(ZnOH)^+ \rightleftarrows Zn^{2+} + OH^-*$$

Amphoteric hydroxides depending on the nature of the reaction partner (an acid or base) can dissociate either like a base (I) or an acid (II). For example:

$$\left.\begin{array}{c} Zn(OH)_2 \rightleftarrows ZnOH^+ + OH^- \\ \downarrow\uparrow \\ Zn^{2+} + OH^- \end{array}\right\} \text{(I)}$$

$$\left.\begin{array}{c} Zn(OH)_2 \rightleftarrows H^+ + HZnO_2^- \\ \uparrow\downarrow \\ [H_2ZnO_2] \rightleftarrows H^+ + ZnO_2^{2-} \end{array}\right\} \text{(II)}$$

The above equations indicate that in the presence of an excess of H^+ ions zinc hydroxide will behave in a solution like a typical base, while in the presence of an excess of OH^- ions it will behave like an acid, therefore the formula H_2ZnO_2 should be used for zinc hydroxide in the second case.

The amphoteric electrolytes (ampholytes) also include $Be(OH)_2$, $Al(OH)_3$, $Pb(OH)_2$, and $Cr(OH)_3$.

The changes in the properties of hydroxides reveal some general laws.

The type of ionization of hydroxides having the general formula MOH depends on the comparative strength and polarity of the M—O and O—H bonds and can proceed in two ways:

$$\begin{array}{c} M—O—H \\ MOH \rightleftarrows M^+ + OH^- \text{ (I)} \\ MOH \rightleftarrows H^+ + MO^- \text{ (II)} \end{array}$$

The alkali metals, alkaline-earth metals, and also the transition elements in low oxidation states (see Sec. 7.1) form ions of a relatively large size

* Zinc hydroxide is a very weak base. In the given case, it has been taken to consider dissociation in steps, which is a property of weak bases. In ionic reactions, on the other hand, zinc hydroxide is always written in the undissociated form.

and with a small charge. For this reason, the M—O bond has a greater polarity than O—H, and the dissociation of MOH is predominantly of the basic type. With an increase in the oxidation state, the covalence of the element-oxygen bond grows, and therefore dissociation is mainly of the acid type, i.e. a hydrogen ion detaches.

If, on the other hand, the polarity of the M—O and O—H bonds is about the same, the hydroxide MOH can dissociate according to either type, basic or acid, i.e. the hydroxide is amphoteric.

Across periods, the radii of ions diminish, while the maximum oxidation state in compounds of the MOH type increases from I to VII. In this connection, the polarizing effect of the ions of elements grows across a period from left to right. Consequently, NaOH has typical basic properties, whereas $HClO_4$ is a typical acid. Aluminium hydroxide exhibits amphoteric properties. If an element forms various hydroxides, for example, $Mn(OH)_2$, $Mn(OH)_3$, $Mn(OH)_4$, H_2MnO_4, and $HMnO_4$ (here the oxidation state of manganese increases from +2 to +7), then in the compounds with lower oxidation states of the relevant element basic properties are more pronounced, while in the compounds with the higher oxidation states, acid properties prevail.

Hence, with an increase in the oxidation state and a decrease in the ionic radius of an element, the acid type of dissociation predominates in hydroxides.

Arrhenius's definition was an important cornerstone for the further development of the theory of acids and bases. These definitions have a number of important shortcomings, however, the main one of which is the limitation of their application only to aqueous solutions of electrolytes.

Questions and Problems

1. Compile a scheme of the dissociation of sulphurous acid by steps. Explain from the standpoint of chemical equilibrium why dissociation in the second step is much weaker than in the first one.

2. Why is KOH a strong base, $Al(OH)_3$ an amphoteric hydroxide, and H_2SO_4 a strong acid?

3. Write equations of the dissociation of the following hydroxides: $Ba(OH)_2$, HNO_3, $H_4P_2O_7$, RbOH, and H_2S. Explain the type of dissociation of each of them.

4. Use the periodic table of elements to determine which of the following bases is the strongest: LiOH, $Mg(OH)_2$, CsOH, $Sr(OH)_2$, $Ca(OH)_2$, and $Ba(OH)_2$. Compile equations of the dissociation of each base.

5. Which of the following binary acids (containing no oxygen) is the strongest: H_2S, H_2Se, HCl, HI? Defend your answer using the periodic table of elements. Write equations of the dissociation of each acid.

5.9. Hydrogen Ion Exponent. The pH of Solutions

It follows from the definitions of the concepts "acid" and "base" that the acidic or alkaline properties of solutions depend on the presence of H^+ or OH^- ions, respectively. Consequently, the acidity or alkalinity of solutions can be characterized quantitatively.

Let us consider the ionization of water, which behaves simultaneously as a donor and acceptor of protons.

The hydrogen atoms in a water molecule are capable of ionization. This is why a water molecule can either donate or accept a proton. This phenomenon is called **autodissociation or autoionization** and can be depicted as follows:

$$2H_2O \rightleftarrows H_3O^+ + :OH^-$$

The process occurs spontaneously, but only to a very small extent. The above equation can be written in a more simplified way:

$$H_2O(lq) \rightleftarrows H^+(aq.) + OH^-(aq.)$$

The dissociation constant is determined by the formula

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

At 22 °C, the dissociation constant of water is 1.8×10^{-16}. This witnesses that water dissociates very slightly.

The concentration of the molecules in liquid water is 55.5 mol/lit and remains practically constant. This enables us to exclude the value of the water concentration from the expression for the dissociation constant. The expression for K can therefore be simplified and acquires the form

$$K(H_2O) = [H^+][OH^-]$$

The constant $K(H_2O)$ is the product of the concentrations of the H^+ and OH^- ions and is called the **ion product of water.** It has been established experimentally that 1×10^{-7} mol dissociates in one litre of water, and equal amounts of the H^+ and OH^- ions form, i.e. 1×10^{-7} mol/lit of each species of ions. Inserting these values into the equation, we obtain

$$K(H_2O) = [H^+][OH^-] = 1.0 \times 10^{-14}$$

This expression for $K(H_2O)$ can be applied not only to pure water, but also to aqueous solutions. Hence, the concentrations of the H^+ and OH^- ions in water are equal, and since each H^+ ion neutralizes only one OH^- ion, the medium will be neutral. Solutions are said to be neutral if the concentrations of the hydrogen and hydroxyl ions are the same and equal 1×10^{-7} mol/lit.

If an acid is added to water, the concentration of H^+ in the solution will grow and therefore it will not equal the concentration of OH^-, but will be higher:

$$[OH^-] = \frac{K(H_2O)}{[H^+]}$$

Since $[H^+]$ increased (an acid was added), then $[OH^-]$ decreased. If a base is added to water, it adds OH^- ions, therefore

$$[H^+] = \frac{K(H_2O)}{[OH^-]}$$

The concentration of H^+ diminishes.

Consequently, when the equality $[H^+] = [OH^-]$ is violated, an increase in $[H^+]$ leads to a decrease in $[OH^-]$ and vice versa.

An increase in the hydrogen ion concentration (the addition of an acid) causes a solution to acquire acidic properties, while an increase in the hydroxyl ion concentration (the addition of an alkali) causes a solution to acquire basic properties:

$[H^+] = [OH^-]$ — a neutral medium
$[H^+] > [OH^-]$ — an acid medium
$[H^+] < [OH^-]$ — a basic medium

If the concentration of one species of the ions grows, the concentration of the other one should lower, but their product must always be 1×10^{-14}. This is why when we know the concentration of one of the ions we can easily calculate that of the other one. For convenience, the negative logarithms of the values of $[H^+]$ and $[OH^-]$ are used instead of their true values.

The negative common logarithm of the concentration of H^+ ions is called the hydrogen ion index or hydrogen ion exponent, but most chemists call it simply the pH, which is its symbol:

$$pH = -\log [H^+]$$

For pure water $pH = -\log (10)^{-7} = 7.0$. The pH decreases when the hydrogen ion concentration grows and increases with an increase in the hydroxyl ion concentration.

Since $K(H_2O) = 1 \times 10^{-14}$, in a neutral solution pH = 7.0, in an acid solution pH < 7.0, and in an alkaline one pH > 7.0. If pH = 4.0, then the hydroxyl ion concentration $pOH = -\log [OH^-] = 14.0 - 4.0 = 10.0$.

The relations between the reaction of a solution, the concentrations of the hydrogen and hydroxyl ions, and the pH are expressed as follows:

$[H^+] = [OH^-] = 10^{-7}$; pH = 7.0; neutral solution
$[H^+] > 10^{-7} > [OH^-]$; pH < 7.0; acid solution
$[H^+] < 10^{-7} < [OH^-]$; pH > 7.0; alkaline solution

The pH is determined with the aid of indicators—organic substances that change their colour in solutions depending on the reaction of the latter. These compounds, e.g. phenolphthalein and methyl orange, are weak acids or bases whose colour in the molecular form differs from that in the ionic form. Assume that the indicator is a weak acid. Hence, the following equilibrium is observed in an aqueous solution:

$$\underset{\text{colourless}}{\text{HInd}} \rightleftarrows \text{H}^+ + \underset{\text{coloured}}{\text{Ind}^-}$$

If this solution is acidified (the concentration of the H^+ ions is increased), equilibrium will shift in the direction of HInd, i.e. the colour of the molecular form of the indicator HInd will be observed. If a base is added to the solution, on the other hand, the concentration of the H^+ lowers ($H^+ + OH^- \rightarrow H_2O$), and therefore equilibrium shifts to the right, i.e. in the direction of the coloured ionized form of the indicator Ind^-.

Example 1. Calculate the concentration of the ions H^+(aq.) in a solution where (a) $[OH^-] = 0.02$ mol/lit, and (b) $[OH^-] = 2.5 \times 10^{-8}$ mol/lit.

Solution.

(a) Since $K(H_2O) = [H^+][OH^-] = 1.0 \times 10^{-14}$, then $[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.02} = 5 \times 10^{-11}$ mol/lit;

(b) $[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-8}} = 4 \times 10^{-8}$ mol/lit.

Example 2. Freshly prepared tomato juice has a pH of about 4.0. Find the concentration of the hydrogen and hydroxyl ions.

Solution. Since $pH = -\log [H^+]$, then $-\log [H^+] = 4.0$. Hence $\log [H^+] = -4.0$. Therefore, $[H^+] = 1 \times 10^{-4}$ mol/lit, and $[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10}$ mol/lit.

Example 3. Determine the pH (a) of a 0.010 mol/lit solution of HCl, and (b) of a 0.010 mol/lit solution of $Ba(OH)_2$.

Solution. (a) HCl is a strong acid. Each mole of HCl in dissociation yields one mole each of H^+ and Cl^-, therefore $[H^+] = 0.010$ mol/lit $= 1 \times 10^-2$, whence $pH = -\log [H^+] = 2.00$

(b) Barium hydroxide, being a strong electrolyte, dissociates by the equation $Ba(OH)_2 \rightleftarrows Ba^{2+} + 2OH^-$. Consequently, each mole of the hydroxide yields two moles of OH^- ions. Therefore, $[OH^-] = 0.02$ mol/lit $= 2 \times 10^{-2}$ mol/lit. Since $K(H_2O) = 1.0 \times 10^{-14}$, then $[H^+] = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-2}} = 5.0 \times 10^{-13}$; $pH = -\log [H^+] = -\log (5.0 \times 10^{-13}) = 12.30$.

Example 4. Find the pH of a solution obtained by mixing equal volumes of a solution of HNO_3 with a concentration of 0.01 mol/lit and 0.0050 mol/lit of a sodium hydroxide solution.

Solution. The mixing of equal volumes of the solutions leads to their dilution, and therefore the concentration of each of the initial substances will be halved, i.e. for HNO_3 it should be 0.0050 mol/lit and for NaOH, 0.0025 mol/lit. But the acid and base react (a neutralization reaction) until one of the reactants is completely used up:

$$HNO_3 + NaOH = NaNO_3 + H_2O$$

It is evident from the initial conditions that the concentration of the NaOH is half that of the HNO_3, and this ratio is retained after dilution. Therefore, after the neutralization of the NaOH, an excess of HNO_3 remains in the solution: 0.0050 − 0.0025 = 0.0025 mol/lit.

The hydrogen ion concentration and pH of the solution are:

$$[H^+] = 0.0025 \text{ mol/lit} = 2.5 \times 10^{-3} \text{ mol/lit}$$
$$pH = -\log 2.5 + 3.0 = 2.6.$$

Questions and Problems

1. What is the relation between the equilibrium constant, dissociation constant, and the law of mass action?

2. Explain why the ion product of water is a constant quantity.

3. What is the reaction of a solution at a pH of 3, 14, 6, and 9? In which solution is the acidity more pronounced and in which is the alkalinity more pronounced?

4. To determine the reaction of a solution, information on the hydrogen ion concentration (pH) is sufficient, while information on the hydroxyl ion concentration (pOH) is not used. Why? Defend your answer.

5. Why can an indicator be used to determine the reaction of a solution?

6*. Find the concentration of H^+ ions and the pH in a solution of NaOH with c = 0.005 mol/lit.

7*. What is the concentration of the H^+ ions in a solution of HNO_3 with c = 0.01 mol/lit? What is the pH of the solution?

8*. To 50 ml of a 10% solution of HCl (a density of 1.047 g/cm^3) there were added 60 ml of an 8% solution of NaOH (a density of 1.109 g/cm^3). What mass of salt formed? What is the reaction of the solution?

5.10. Hydrolysis of Salts

Salts are electrolytes that form cations of a metal and anions of an acid residue when they dissociate.

Salts decompose into ions in a solution differently depending on their type.

Neutral (normal) salts form a metal cation and an acid residue anion:

$$Na_2SO_4 \rightleftarrows 2Na^+ + SO_4^{2-}$$

Acid salts form a metal cation and an acid anion:

$$NaHCO_3 \rightleftarrows Na^+ + HCO_3^-$$

The hydrogen carbonate anion in an alkaline solution, in turn, can dissociate:

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$$

Basic salts dissociate with the formation of a hydroxo cation:

$$Mg(OH)Cl \rightleftarrows MgOH^+ + Cl^-$$

One of the important chemical properties of salts is hydrolysis.

Measurement of the pH of salt solutions shows that they may have a neutral, acid, or alkaline reaction. For instance, solutions of Na_2CO_3 have an alkaline reaction (pH > 7.0), while solutions of $Al_2(SO_4)_3$ have an acid one (pH < 7.0). These compounds do not contain H^+ or OH^- ions, hence the acid-base properties of salt solutions are due to the properties of the cations and anions formed when they dissociate.

When many salts are dissolved in water, the salt ions react chemically with the H^+ and OH^- ions of the water to form weak electrolytes. Depending on the nature of the initial salt, either H^+ or OH^- ions accumulate in the solution, and the latter accordingly acquires an acid or alkaline reaction.

The process of the reaction of salt ions with water resulting in the formation of a weak electrolyte is called hydrolysis.

As a result of hydrolysis, the equilibrium of electrolytic dissociation of water shifts. The essence of this process consists in that the salt cation or anion binds the OH^- or H^+ ions, respectively, with the formation of a weak electrolyte (base or acid).

Considering salts as products of the reaction of an acid and base, we can divide them into four types depending on the strength of the initial acid or base: (1) salts formed by a strong base and strong acid; (2) salts formed by a strong base and weak acid; (3) salts formed by a weak base and strong acid; and (4) salts formed by a weak base and weak acid.

A Salt Formed by a Cation of a Strong Base and an Anion of a Strong Acid. Salts of this type do not hydrolyze because no weak electrolyte can form when they interact with water. Consequently, the equilibrium of dissociation of the water is not disturbed, and therefore solutions of such salts have a neutral reaction (pH = 7.0).

A Salt Formed by a Cation of a Strong Base and an Anion of a Weak Acid. Hydrolysis of this type of salts is also known as anion or alkaline hydrolysis. Let us consider the hydrolysis of Na_2CO_3 as an example. When this salt is dissolved in water, the CO_3^{2-} ions combine with the hydrogen ions of the water to form weakly dissociating HCO_3^- ions:

~~$2Na^+ + CO_3^{2-} + HOH \rightleftarrows 2Na^+ + HCO_3^- + OH^-$ (step I)~~

$$CO_3^{2-} + HOH \rightleftarrows HCO_3^- + OH^-$$

$$Na^+ + HCO_3^- + H_2O \rightleftarrows H_2CO_3 + Na^+ + OH^- \quad \text{(step II)}$$

$$HCO_3^- + HOH \rightleftarrows H_2CO_3 + OH^-$$

It should be stressed that the second step of hydrolysis does not almost proceed because the increase in the hydroxide ion concentration in the solution shifts equilibrium to the left.

Hence, the given case of hydrolysis is a typical reversible reaction.

In the molecular form, the hydrolysis equation is as follows:

$$Na_2CO_3 + HOH \rightleftarrows NaHCO_3 + NaOH$$

The second step of hydrolysis is disregarded.

Consequently, each hydrogen ion neutralizes one negative charge of the acid residue ion CO_3^{2-}, and a hydroxide ion is liberated from a water molecule. An excess of hydroxide ions forms that imparts an alkaline reaction to the solution (pH > 7.0).

Hence, solutions of salts formed by a strong base and a weak acid have an alkaline reaction.

A Salt Formed by a Cation of a Weak Base and an Anion of a Strong Acid. Hydrolysis of this type of salts is also known as cation or acid hydrolysis. Let us consider the hydrolysis of $CuCl_2$. It is due to the formation of weakly dissociating ions $(CuOH)^+$:

$$Cu^{2+} + 2Cl^- + H_2O \rightleftarrows [Cu(OH)]^+ + 2Cl^- + H^+ \text{ (step I)}$$
$$Cu^{2+} + H_2O \rightleftarrows CuOH^+ + H^+$$
$$CuOH^+ + Cl^- + H_2O \rightleftarrows Cu(OH)_2 + H^+ + Cl^- \text{ (step II)}$$
$$CuOH^+ + H_2O \rightleftarrows Cu(OH)_2 + H^+$$

In the molecular form, the hydrolysis equation is as follows:

$$CuCl_2 + HOH \rightleftarrows CuOHCl + HCl$$

The first step of this hydrolysis reaction is also more pronounced. An excess of hydrogen ions is observed in the solution. Consequently, solutions of salts formed by a weak base and a strong acid have an acid reaction (pH < 7.0). This case of hydrolysis is also reversible.

A Salt Formed by a Cation of a Weak Base and an Anion of a Weak Acid. Hydrolysis of this type of salts is also known as cation-anion hydrolysis. In a salt of a weak base and a weak acid such as aluminium sulphide Al_2S_3, the cation behaves like an acid and the anion like a base:

$$Al_2S_3 + 6H_2O = 2Al(OH)_3\downarrow + 3H_2S\uparrow$$

The reaction proceeds virtually to the end, and hydrolysis is irreversible. The reaction and pH of solutions of salts formed by a weak base and a weak acid depend on the relative strength of the formed weak acids and bases and can be either neutral or insignificantly displaced in either direction, i.e. weakly acidic or weakly alkaline.

Hydrolysis is substantially affected by the concentration and temperature. On the basis of Le Chatelier's principle, let us see how these factors affect the position of hydrolytic equilibrium. Dilution of the solution is equivalent to an increase in the concentration of one of the reactants (water in the given case). Therefore equilibrium shifts to the right, i.e. hydrolysis

grows. Conversely, the hydrolysis of concentrated solutions proceeds much more weakly.

A change in the temperature affects hydrolysis because of the pronounced temperature dependence of the degree of water dissociation. With elevation of the temperature, the concentration of H^+ and OH^- ions in the solution sharply grows. This increases the probability of their combination with the formation of a weakly dissociating acid or base. This is why hydrolysis proceeds more completely with elevation of the temperature. This conclusion is confirmed by the fact that a neutralization reaction is exothermic. Since hydrolysis is the opposite of neutralization, i.e. is endothermic, by Le Chatelier's principle heating increases hydrolysis.

Questions and Problems

1. Which of the following salts is subjected to hydrolysis: $Al_2(SO_4)_3$, $FeCl_3$, K_2CO_3, K_2S?

2. Which of the following salts, namely, $AlCl_3$, K_2CO_3, Na_2SO_4, $NaNO_3$, $FeCl_2$, $ZnSO_4$, and K_2S experiences (a) only cation hydrolysis; (b) only anion hydrolysis? Compile the ionic equations. Indicate the reaction of the solutions.

3. Write the molecular and ionic equations of the hydrolysis of $FeCl_3$. What is the reaction of this solution?

4. Why does a precipitate of aluminium hydroxide form when aluminium chloride reacts with sodium carbonate?

5*. In 46.52 ml of water, there were dissolved 3.48 g of a mixture of copper nitrate and copper sulphate. When an excess of a barium chloride solution was added to the above solution, 2.33 g precipitated. Determine the composition of the initial mixture of $Cu(NO_3)_2$ and $CuSO_4$ in per cent, and also the per cent concentration by mass of each of the salts in the obtained solution.

SUMMARY

Solutions are homogeneous systems of a variable composition consisting of two and more components. The component present in a greater amount and retaining its phase state in the formation of a solution is called a solvent. The other component or components are called solutes. The relative content of the solute and solvent is indicated by using the terms dilute and concentrated solutions, but they are only a qualitative characteristic. The quantitative composition of a solution is determined by its concentration. The concentration of a solute in a saturated solution is called its solubility.

The process of dissolution may be attended by lowering or elevation of the solution's temperature. The heat energy evolved or absorbed in the dissolution of solutes is called their heat of solution. Aqueous solutions of salts, acids, and bases exhibit electrical conductance. Substances whose aqueous solutions conduct an electric current are called electrolytes, and their decomposition into ions is called electrolytic dissociation. The latter

is described quantitatively by the degree of dissociation that shows the strength of an electrolyte. The properties of solutions are generally appraised by the ratio of the H^+ and OH^- ion concentration in them.

When salts are dissolved in water, hydrolysis may occur, i.e. the reaction of the salt ions with water yielding a weak electrolyte. This process is determined first of all by the nature of the salt itself.

CHAPTER 6

BASIC CLASSES OF INORGANIC COMPOUNDS AND THEIR NOMENCLATURE

OBJECTIVES

To know the most important classes of inorganic compounds—oxides, bases, acids, and salts; the ways of their preparation and typical chemical properties, and also the nomenclature of these compounds.

6.1. Oxides

Oxides are binary compounds in which one of the elements is oxygen in the oxidation state -2.

The following rules are adhered to in the nomenclature of oxides:

(1) when writing formulas, oxygen is always put in the second place—NO, CaO;

(2) the same order is followed when naming oxides—BaO is barium oxide, and K_2O is potassium oxide.

(3) if an element can form several oxides, the name of the element is followed by its oxidation state (number), for example, N_2O_5 is nitrogen(V) oxide, N_2O is nitrogen(I) oxide, FeO is iron(II) oxide, and Fe_2O_3 is iron(III) oxide;

(4) the number of atoms of each element in an oxide can be indicated by using the Greek prefixes mono-, di-, tri-, tetra-, penta-, hexa-, etc. for 1, 2, 3, 4, 5, 6, etc. with them. For instance, N_2O is dinitrogen oxide, NO is nitrogen monoxide, NO_2 is nitrogen dioxide, and N_2O_5 is dinitrogen pentoxide. The prefix mono-, however, is generally omitted with the first element, e.g. CO is carbon monoxide, and CO_2 is carbon dioxide.

(5) it is recommended to name the anhydrides of inorganic acids as oxides, for example, N_2O_5 should be called nitrogen(V) oxide, and not nitric acid anhydride.

Preparation. Oxides can be produced in several ways.

1. By reacting simple substances with oxygen. Simple substances when heated frequently become oxidized with the evolution of light and heat. This process is called burning or combustion:

$$C + O_2 = CO_2$$

2. By oxidizing compounds with the formation of oxides of the elements contained in the initial compound:

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

3. By the decomposition of nitrates, carbonates, and hydroxides:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$
$$CaCO_3 = CaO + CO_2$$
$$Cu(OH)_2 = CuO + H_2O$$

4. By oxidizing metals using oxides of other metals. Such reactions underlie the thermal reduction method—the reduction of metals from their oxides by more active metals:

$$2Al + Cr_2O_3 = 2Cr + Al_2O_3$$

5. By decomposing higher oxides or additionally oxidizing lower oxides:

$$4CrO_3 = 2Cr_2O_3 + 3O_2$$
$$4FeO + O_2 = 2Fe_2O_3$$
$$2CO + O_2 = 2CO_2$$

Salt-forming and **indifferent** oxides are distinguished. The latter include oxides forming neither acids nor bases (e.g., N_2O and NO).

The salt-forming oxides are further divided into **basic, acid,** and **amphoteric** ones.

Basic Oxides. Bases correspond to these oxides. For instance, Na_2O, CaO, and MgO are basic oxides because the bases NaOH, $Ca(OH)_2$, and $Mg(OH)_2$ correspond to them. Some oxides (K_2O and CaO) readily react with water to form the relevant bases (hydroxides):

$$CaO + H_2O = Ca(OH)_2$$
$$K_2O + H_2O = 2KOH$$

The oxides Fe_2O_3, CuO, and Ag_2O do not react with water, but they neutralize acids, therefore they are considered to be basic:

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O$$
$$Ag_2O + 2HNO_3 = 2AgNO_3 + H_2O$$

A typical chemical property of basic oxides is their reaction with acids, generally to form a salt and water:

$$FeO + 2HCl = FeCl_2 + H_2O$$

Basic oxides also react with acid oxides:

$$CaO + CO_2 = CaCO_3$$

Acid Oxides. Acids correspond to these oxides. For example, nitrous acid HNO_2 corresponds to the oxide N_2O_3, perchloric acid $HClO_4$ corresponds to Cl_2O_7, and sulphuric acid H_2SO_4 corresponds to SO_3.

A typical chemical property of acid oxides is their reaction with bases to form a salt and water:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

Most acid oxides react with water to form the relevant acids. At the same time, the oxide SiO_2 is virtually insoluble in water, but it neutralizes bases, and therefore it is an acid oxide:

$$2NaOH + SiO_2 \overset{\text{fusion}}{=} Na_2SiO_3 + H_2O$$

Amphoteric Oxides. These are oxides which depending on the conditions exhibit either basic or acid properties. In other words, when reacting with acids they behave like basic oxides, and when reacting with bases, like acid oxides.

Not all amphoteric oxides react with bases and acids to the same extent. Some of them have more pronounced basic properties, and others have more pronounced acid properties.

If zinc or chromium oxide reacts with acids and bases to the same extent, then the oxide Fe_2O_3 has mainly basic properties.

We shall show the properties of amphoteric oxides using ZnO as an example:

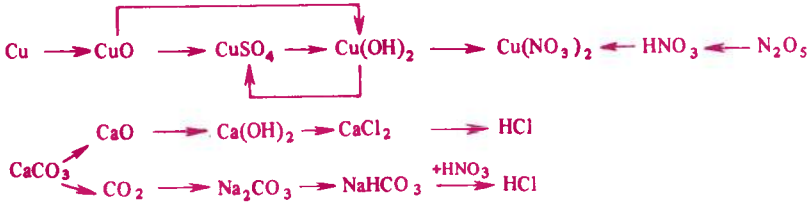
$$ZnO + 2HCl = ZnCl_2 + H_2O$$

$$ZnO + 2NaOH = Na_2ZnO_2 + H_2O$$

Questions and Problems

1. What is the relation between (a) a base and an acid; (b) a basic oxide and a base; (c) a metal and a basic oxide; (d) an acid oxide and an acid; (e) a basic oxide and an acid; (f) an acid oxide and a base; (g) an acid and a salt; (h) a base and a salt; (i) a basic oxide and an acid oxide? Defend your answer using reaction equations.

2. How can the following transformations be conducted:



3. A reaction proceeds between 20 g of CaO and 20 g of CO_2. What salt forms and how many grammes? Confirm your answer by calculations.

4. What amount of potassium hydroxide is needed to react with 1.02 g of Al_2O_3?

5. How many litres of CO_2 will be evolved if 200 g of $CaCO_3$ containing 15% of impurities are roasted?

6.2. Bases

The formulas of bases reflect the type of their dissociation, namely, an atom of a metal is bound to one or several hydroxyl groups.

Hydroxides are named by adding the word hydroxide to the name of the relevant metal; e.g. NaOH is sodium hydroxide, and $Ca(OH)_2$ is calcium hydroxide. If a metal forms hydroxides of different compositions, the name of the metal is followed by its oxidation state in parentheses, e.g. $Fe(OH)_2$ is iron(II) hydroxide, and $Fe(OH)_3$ is iron(III) hydroxide.

The hydroxides of the alkali and alkaline-earth metals such as KOH, NaOH, and $Ba(OH)_2$ are called **alkalies**.

The number of hydroxyl groups determines the atomicity or acidity of a base, i.e. the ability of the base to neutralize acids. For instance, NaOH is a monoatomic or monoacid base, and $Ca(OH)_2$ is a diatomic or diacid base because in a neutralization reaction of these bases with a monoatomic or monobasic acid (e.g., HCl) one or two moles of HCl are used per mole of the relevant base. These reactions follow the equations:

$$NaOH + HCl = NaCl + H_2O$$

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$

Preparation*.

1. By reacting basic oxides with water:

$$CaO + H_2O = Ca(OH)_2$$

2. By reacting metals with water:

$$2Na + 2H_2O = 2NaOH + H_2$$

$$Ca + 2H_2O = Ca(OH)_2 + H_2$$

* When writing the equations of reactions showing the ways of preparation or the properties of various classes of substances, do not forget to use the solubility table (see Appendix 3).

3. By an exchange reaction between salts and bases:

$$CuSO_4 + 2NaOH = Cu(OH)_2\downarrow + Na_2SO_4$$

The third way yields bases that are insoluble in water, i.e. that cannot be prepared by the first or second ways.

4. By the electrolysis of aqueous solutions of salts and alkali metals. For this way, see Sec. 7.5.

Physical Properties. Bases are solid crystalline substances that dissolve differently in water. Some of them dissolve very readily. They include the hydroxides of the alkali and alkaline-earth metals: LiOH, NaOH, KOH, CsOH, RbOH, FrOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$. The other hydroxides have a poor solubility.

Aqueous solutions of the alkalies have a soapy feeling, erode the skin and fabrics, etc. In this connection, they are called caustic alkalies.

Chemical Properties. Solutions of bases have a pH exceeding seven and change the colour of indicators, namely, litmus to blue, phenolphthalein to crimson, and methyl orange to yellow. This property is widely used to find the pH of solutions. But only soluble bases react with indicators in this way.

Soluble bases readily react with acids (a neutralization reaction):

$$NaOH + HCl = NaCl + H_2O$$

with acid and amphoteric oxides:

$$2KOH + ZnO = K_2ZnO_2 + H_2O$$

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$

with salts

$$Ba(OH)_2 + Na_2SO_4 = BaSO_4\downarrow + 2NaOH$$

Insoluble bases react appreciably only with acids:

$$Cu(OH)_2 + H_2SO_4 = CuSO_4 + 2H_2O$$

and with acid oxides:

$$Cu(OH)_2 + SO_3 = CuSO_4 + H_2O$$

Among the other chemical properties of bases, mention should be made of their attitude to heating. Many insoluble bases when heated decompose to form the relevant oxide and water:

$$Cu(OH)_2 = CuO + H_2O$$

Some bases decompose only when roasted:

$$Ca(OH)_2 = CaO + H_2O$$

The alkali metal hydroxides are stable when heated.

Questions and Problems

1. Name the bases whose formulas are given below: $NaOH$, $Fe(OH)_3$, $Fe(OH)_2$, $Cu(OH)_2$, $Ba(OH)_2$, $CsOH$, KOH, $Mg(OH)_2$, and $Ca(OH)_2$. Which of them are soluble and which are not? Compile the equations of dissociation of the soluble bases. What can you say about the pH of their solutions?

2. With which of the following substances will barium hydroxide react: CO_2, SO_3, H_2O, O_2, HNO_3, $NaOH$, Fe_2O_3, $Fe(OH)_3$, H_2SO_3, Al_2O_3, and ZnO? Compile the molecular and ionic equations of these reactions.

3. Which of the following bases can be obtained by reacting the relevant oxide with water: KOH, $NaOH$, $Cu(OH)_2$, $Pb(OH)_2$, $Ca(OH)_2$, $Cr(OH)_3$, and $LiOH$? Write the equations of the possible reactions.

4[a]. What mass of a 10% sodium hydroxide solution is needed to neutralize 40 g of a 10% sulphuric acid solution? What mass of salt forms?

5[a]. Determine the per cent concentration by mass of sodium hydroxide in a solution if it is known that 50 g of the solution completely "dissolve" 10.8 g of aluminium.

6.3. Acids

The number of hydrogen ions formed in the dissociation of a molecule determines the atomicity or basicity of acids. Accordingly, we distinguish monoatomic or monobasic (HCl, HNO_3), diatomic or dibasic (H_2SO_4, H_2S), and polyatomic or polybasic (H_3PO_4) acids. Depending on the elemental composition, we distinguish two types of acids: **oxyacids** and **binary** ones (hydracids).

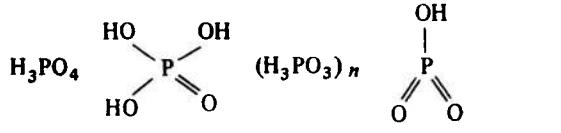
The name of an acid is formed from that of its characteristic atom. In anhydrous binary acids, the acid residue is given the suffix *-ide*, and the entire molecule is considered as a binary compound of hydrogen in which the latter is the electropositive component. For example, HCl is hydrogen chlor*ide*, H_2S is hydrogen sulph*ide*, and HCN is hydrogen cyan*ide* (here the CN^- ion acts like a simple non-metal anion). Aqueous solutions of these acids are named by adding the prefix *hydro-* to the name of the characteristic element and replacing the suffix *-ide* by *-ic acid*, e.g. *hydro*chlor*ic acid*, *hydro*sulphur*ic acid*, and *hydro*cyan*ic acid*.

Oxyacids (also called ternary acids) contain binary anions (the electronegative components). Their general formula is H_mXO_n, where X is the central or characteristic element giving the acid its name, and m and n are integers. The central element may exist in different oxidation states, and there may be an acid corresponding to each state. These conditions are denoted by using various prefixes and suffixes, namely, the prefixes *hypo-* and *per-*, and the suffixes *-ous* and *-ic*. When the characteristic element has only a single oxidation state, the suffix *-ic* is used (bor*ic* acid H_3BO_3). When it has two oxidation states, the suffix *-ous* denotes the lower one, and *-ic* the higher one (sulphur*ous* acid H_2SO_3 and sulphur*ic* acid H_2SO_4). When the characteristic element has three oxidation states, the prefix *hypo-*

is used together with the suffix *-ous* for the lowest one, only the suffix *-ous* for the middle one, and the suffix *-ic* for the highest one (*hypo*phosphor*ous* acid H_3PO_2, phosphor*ous* acid H_3PO_3, and phosphor*ic* acid H_2PO_4). With four oxidation states, the sequence is *hypo-* and *-ous*, *-ous*, *-ic*, and *per-* and *-ic* (hypochlor*ous* acid HClO, chlor*ous* acid $HClO_2$, chlor*ic* acid $HClO_3$, and *per*chlor*ic* acid $HClO_4$).

The anions of oxyacids are named by retaining the prefix, if any, and using the suffix *-ite* instead of *-ous* and *-ate* instead of *-ic* (SO_3^{2-} is sulph*ite*, SO_4^{2-} is sulph*ate*, ClO_4^- is perchlor*ate*, etc.).

The prefixes *ortho-* and *meta-* are used to designate acids with the same characteristic element in the same oxidation state, but differing in the number of hydroxy groups:



orthophosphoric acid metaphosphoric acid

Preparation. Binary acids are generally prepared in two ways, either by the direct reaction of a non-metal with hydrogen:

$$H_2 + Cl_2 = 2HCl$$

or by the action of stronger acids on the relevant salts:

$$FeS + 2HCl = FeCl_2 + H_2S\uparrow$$
$$FeS + 2H^+ + 2Cl^- = Fe^{2+} + 2Cl^- + H_2S\uparrow$$

Most oxyacids are prepared by reacting the relevant oxides with water:

$$SO_3 + H_2O = H_2SO_4$$
$$P_2O_5 + 3H_2O = 2H_3PO_4$$

Consequently, the oxyacids are also hydroxides, but of non-metals.

Physical Properties. Under ordinary conditions, acids are liquid (H_2SO_4, HNO_3, $HClO_4$, etc.) or solid (H_3PO_4) substances. Most acids mix with water in any proportions; the solutions have an acid taste and erode the skin and fabrics. All acid solutions have a pH under seven and therefore change the colour of litmus to red, of methyl orange to pink, while phenolphthalein remains colourless.

Chemical Properties. Most acids in aqueous solutions react with metals. In these reactions, the hydrogen is replaced by a metal atom, i.e. the hydrogen ions are an oxidizing agent:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow$$

or in the ionic form

$$Zn + 2H^+ + 2Cl^- = Zn^{2+} + 2Cl^- + H_2\uparrow$$
$$Zn + 2H^+ = Zn^{2+} + H_2$$

$$Fe + H_2SO_4(dil.) = FeSO_4 + H_2\uparrow$$
$$Fe + 2H^+ = Fe^{2+} + H_2\uparrow$$

But not all metals behave identically with dilute acids. If we compare the metals with one another, we shall see that each of them has a different chemical activity as regards its ability to displace hydrogen. Here we obtain what is known as the electromotive (or electrochemical) series of metals (see p. 141).

Each of the metals to the left of hydrogen (when the series is arranged horizontally) in the series can displace hydrogen from an acid.

Therefore, metals such as mercury, copper, silver, and gold do not displace hydrogen from acids.

Acids also react with bases, with basic and amphoteric oxides:

$$2HCl + CuO = CuCl_2 + H_2O$$
$$H_2SO_4 + ZnO = ZnSO_4 + H_2O$$

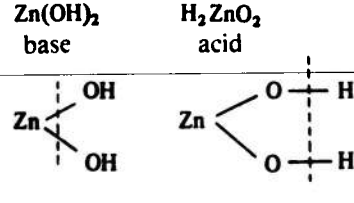
and also with salts

$$BaCl_2 + H_2SO_4 = BaSO_4\downarrow + 2HCl$$

Amphoteric Hydroxides. These hydroxides react with both bases and acids:

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$
$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

Consequently, zinc hydroxide can be represented in either of two forms—a basic and an acid one:



Questions and Problems

1. Name the following acids: HNO_2, H_2SO_4, H_2SiO_3, H_2SO_3, H_2S, H_2CO_3, H_3PO_4, HCl, and HBr. Write the equations of their dissociation. Classify these acids by their composition and basicity. What can you say about the pH of their solutions?

2. With which of the following substances does sulphuric acid react: KOH, CuO, $Ba(OH)_2$, Fe_2O_3, Al_2O_3, $Al(OH)_3$, CO_2, SiO_2, PbO, H_3PO_4, Cu, Fe, H_2O, and O_2? Write the equations of the possible reactions in the molecular and ionic forms.

3. What oxides correspond to the acids HNO_3, HNO_2, H_2SO_3, H_2SO_4, H_2CO_3, H_2SiO_3, H_3PO_4?

4. What products can be obtained when sulphuric acid is reacted with (a) sodium chloride, and (b) sodium sulphate?

5[a]. What is the per cent concentration by mass of zinc chloride in a solution prepared by reacting 13 g of metallic zinc with 100 g of a solution containing 14.6 g of HCl?

6[a]. What mass of a 20% HCl solution was used for the complete "dissolution" of 10 g of a mixture of zinc with zinc oxide if it is known that 2.24 lit of hydrogen was evolved?

7[a]. Calculate the per cent concentration by mass of sulphuric acid in a solution obtained by dissolving 40 g of SO_3 in 160 g of an 80% solution of H_2SO_4?

8. When sulphuric acid was reacted with 800 g of NaCl, 200 g of HCl were obtained. What is the mass fraction (%) of the product with respect to the theoretical yield?

9[a]. How many millilitres of a KOH solution with a concentration of $c = 0.2$ mol/lit are needed to neutralize 20 ml of an HCl solution with $c = 0.1$ mol/lit?

10[a]. To 25 ml of a 10% HCl solution (density = 1.047 g/cm^3) there were added 30 ml of a 10% NaOH solution (density = 1.109 g/cm^3). What was the reaction of the solution after completion of the reaction?

6.4. Salts

Salts can be considered as a product of the complete or partial replacement of the hydrogen atoms in an acid molecule by a metal, or as a product of the complete or partial replacement of the hydroxyl groups in a molecule of a base by an acid residue. For example, two salts can be obtained from sulphuric acid H_2SO_4 when replacing the hydrogen by sodium, namely, Na_2SO_4 (the product of complete replacement of hydrogen by sodium atoms) and $NaHSO_4$ (the product of partial replacement of hydrogen). Other examples are $AlOHCl_2$ and $AlCl_3$, $Cr(OH)_2NO_2$ and $Cr(NO_3)_3$. Depending on their composition, **normal (neutral)**, **acid**, and **basic** salts are distinguished.

Normal salts such as $Ca_3(PO_4)_2$, $MgSO_4$, and K_2SO_4 should be considered as products of the complete replacement of the hydrogen atoms in an acid molecule.

Acid salts such as $Ca(H_2PO_4)_2$, $CaHPO_4$, and $NaHSO_4$ are products of incomplete, or partial replacement of the hydrogen atoms in an acid molecule by a metal atom.

Basic salts such as $Al(OH)SO_4$ and MgOHI can be considered as a product of the partial replacement of the hydroxyl groups in a base molecule by an acid residue.

If one metal and two acids participate in the formation of a salt, it is called **mixed**, while if two metals and one acid form a salt, it is called **double**.

In formulas of salts, the electropositive component (cation) is always written first.

Monoatomic anions are named by the element forming them with the addition of the suffix *-ide*:

H^- is hydr*ide*	O^{2-} is ox*ide*
F^- is fluor*ide*	S^{2-} is sulph*ide*
Br^- is brom*ide*	Cl^- is chlor*ide*

How the anions of oxyacids are named has been indicated on p. 117. Examples are:

NO_2^-—nitrite	ClO^-—hypochlorite
NO_3^-—nitrate	ClO_2^-—chlorite
SO_3^{2-}—sulphite	ClO_3^-—chlorate
SO_4^{2+}—sulphate	ClO_4^-—perchlorate

Salts are named in the same order as their formula is written—first the cation is indicated, and then the anion:

NaCl is sodium chloride	PbS is lead sulphide
$CaSO_4$ is calcium sulphate	K_2SO_3 is potassium sulphite

If a metal exhibits different oxidation states, when writing the names of the relevant salts the oxidation state is indicated by a Roman numeral:

$FeCl_2$ is iron(II) chloride	$CuSO_4$ is copper(II) sulphate
$FeCl_3$ is iron(III) chloride	

In naming acid salts, *hydrogen* is added to the name of the oxyanion, and a prefix is used to indicate the number of hydrogen atoms in the molecule:

$NaHCO_3$ is sodium *hydrogen* carbonate

$Ca(H_2PO_4)_2$ is calcium *dihydrogen* phosphate

In naming basic salts, *hydroxide* is added to the name of the oxyanion, e.g. MgOHCl is magnesium *hydroxide* chloride. Only diatomic, triatomic and polyatomic acids can form acid salts, and diatomic, triatomic, and polyatomic bases can form basic salts.

When writing the structural formula of salts, the hydrogen atoms in the relevant acid are replaced by atoms of a metal. Examples of writing the structural formulas of acids and salts corresponding to them are given in Table 3.

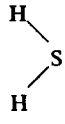
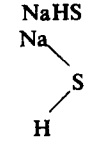
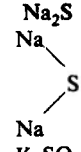
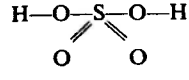
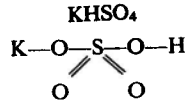
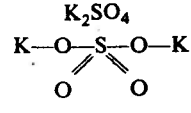
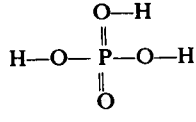
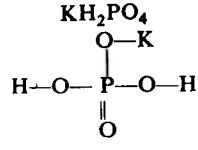
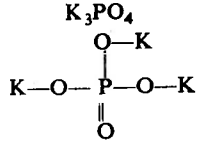
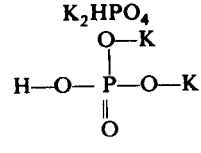
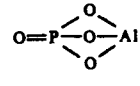
Preparation. We can single out a broad group of reactions that can be used to produce salts, but when choosing them account must be taken first of all of the economical aspect. The following examples do not always comply with this requirement, but in addition to their theoretical significance they indicate the possibility of obtaining salts. This is achieved by reacting:

(1) metals with non-metals:

$$Mg + Cl_2 = MgCl_2$$

Table 3

Examples of the Structural Formulas of Acids and Salts Corresponding to Them

Acid	Structural formula	Acid salt	Normal salt
H_2S		$NaHS$ 	Na_2S 
H_2SO_4		$KHSO_4$ 	K_2SO_4 
H_3PO_4		KH_2PO_4 	K_3PO_4 
		K_2HPO_4 	$AlPO_4$ 

(2) metals with acids:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow$$

(4) basic oxides with acids:

$$CaO + 2HCl = CaCl_2 + H_2O$$

(3) metals with salts:

$$Cu + HgCl_2 = CuCl_2 + Hg$$

(5) acid oxides with bases:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

(6) acids with bases:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

(7) acid oxides with bases:

$$CaO + CO_2 = CaCO_3$$

(8) salts with salts:

$$AgNO_3 + NaCl = AgCl\downarrow + NaNO_3$$

(9) salts with bases:

$$CuSO_4 + 2NaOH = Cu(OH)_2\downarrow + Na_2SO_4$$

(10) salts with acids:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl\uparrow$$
$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2\uparrow$$

Acid salts are mainly prepared in the same ways as normal ones, but here it is important to ensure the proper molar ratios of the reactants. For example, when NaOH and H_2SO_4 are taken in a molar ratio of 2:1, a normal salt forms:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

whereas when they are taken in a ratio of 1:1, an acid salt forms:

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O$$

When NaOH and CO_2 are taken in a molar ratio of 2:1, a normal salt forms:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

whereas with a ratio of 1:1, an acid salt forms:

$$NaOH + CO_2 = NaHCO_3$$

When an excess of an acid reacts with a normal salt, it transforms the latter into an acid one:

$$Ca_3(PO_4)_2 + H_3PO_4 = 3CaHPO_4$$

or

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$$

Physical Properties. Salts are solid crystalline substances with high melting points. With respect to their solubility in water, we distinguish readily soluble (NaCl, KCl, $CaCl_2$), sparingly soluble ($PbCl_2$, $CaSO_4$, Ag_2SO_4), and virtually insoluble ($BaSO_4$, $PbSO_3$, $CaCO_3$) salts.

Chemical Properties. Salts react with metals, acids, bases, and with one another. Such reactions were illustrated when discussing the ways of preparing salts (see reactions 3, 8, 9, and 10).

Some salts of the oxyacids decompose when roasted. This property is used to obtain oxides (see Sec. 6.1).

Questions and Problems

1. Name the salts $NaHSO_3$, Na_2SO_4, CuS, and $Ca(HCO_3)_2$. Indicate the ways of preparing them.

2. With which of the following substances will sulphuric acid enter into a reaction: Na_2CO_3, K_2SO_4, $Cu(OH)_2$, $BaCl_2$, and NaCl? Compile the molecular and ionic equations of these reactions.

3. What salt and how many grammes of it form when 20 g of NaOH are reacted with 30 g of H_2SO_4?

4. Through a solution containing 14.8 g of $Ca(OH)_2$ there were passed 22.4 lit of CO_2. What was the composition and mass of the salt formed?

SUMMARY

In inorganic chemistry, all substances are divided into four most important classes: oxides, bases, acids, and salts.

Oxides are binary compounds with oxygen being one of the two elements in the compound. Basic, acid, and amphoteric oxides are distinguished. Bases correspond to basic oxides, acids to acid ones, while amphoteric oxides have a dual nature.

Bases and acids are compounds that are diametrically opposite in their properties. They react with one another to form a salt and water. Such a reaction is called neutralization. Depending on the amount of each compound taken for a reaction between a polyatomic acid and a base, the salt formed can be normal, acid, or basic.

There is a genetic relation between simple and compound substances—their mutual conversion is possible under certain conditions: it is possible to produce oxides from simple substances, the oxides can be transformed into bases, acids, and salts. Salts, in turn, can be transformed into bases, acids, oxides, and metals.

CHAPTER 7

OXIDATION-REDUCTION REACTIONS

OBJECTIVES

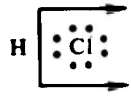
To determine the oxidation state of atoms in molecules of simple and compound substances; to explain the essence of the oxidation and reduction processes; to compile equations by the methods of electron balance and half-reactions.

7.1. Oxidation State of an Element

When treating the types of a chemical bond, we showed that the formation of an ionic bond is preceded by the transfer of electrons from one set of atoms to another, the result being the formation of charged particles (cations and anions). The loss of electrons by an atom (ion, molecule) is called **oxidation**, and the gain of electrons, **reduction**.

When a polar covalent bond forms between atoms in a molecule, the transfer of the bonding electrons in the direction of the more electronegative atom will cause the latter to have an excess of a negative charge. The more electropositive atom, conversely, will experience a lack of electrons. The example of hydrogen chloride reveals that the hydrogen atom carries a positive charge, and the chlorine atom carries a negative charge of the same magnitude. The effective charge on each of these atoms, however, is less than a unit charge of an electron.

When we have to do with the formal counting of the electrons belonging in this case to each of the atoms, for simplification the bonding pair of electrons is considered to belong to the more electronegative chlorine atom:



This assumption signifies that chlorine now has eight electrons, while hydrogen is deprived of an electron, i.e. we must conditionally ascribe the charge -1 to chlorine, and $+1$ to hydrogen.

The conditional electric charge ascribed to an atom when assuming that the molecule containing it is constructed according to the ionic type is called the oxidation number or oxidation state of this atom.

The terms **oxidation number** and **oxidation state** are often used interchangeably, although there is a slight difference between them. Oxidation state usually describes what the oxidation number is in a particular compound. For instance, in $CuCl_2$, the oxidation number of the copper is $+2$, therefore, in this compound copper is in the $+2$ oxidation state.

For molecules with a covalent type of bond, it is conditionally assumed that the electron pairs bonding a given atom to another one are completely shifted toward the more electronegaive atom.

Rules for Determining the Oxidation State. The oxidation state can be determined for every atom in any compound in accordance with definite rules whose essence is as follows.

1. In simple substances (N_2, Cl_2, O_2, H_2, etc.), the electrons are shared equally by like atoms, i.e. there is no displacement of the bonding electrons, therefore the oxidation state of the atoms is 0.

2. The oxidation state of a monoatomic (simple) ion such as Ca^{2+} coincides with the charge of the ion (+2 in the given case).

3. In all their compounds, the alkali metals have an oxidation state of +1, and the alkaline-earth ones of +2.

4. Hydrogen in compounds with non-metals has an oxidation state of +1, while in salt-forming hydrides (CaH_2, NaH, etc.), its oxidation state is −1.

5. Fluorine is the most electronegative element; in compounds with other elements its oxidation state is −1.

6. Oxygen exhibits an oxidation state of −2 in its compounds. An exception is OF_2, where the oxidation state of oxygen is +2, and of fluorine is −1.

7. The sum of the oxidation states of all the atoms in an ion determines the total charge of this particle. This enables one to find unknown oxidation states of various atoms in a molecule. Let us consider the NO_3^- ion as an example. By the above rules, the oxidation state of oxygen is −2, while this ion includes a total of three oxygen atoms, and their formal charge is 3 × (−2). Consequently, the nitrogen in this compound has an oxidation number of +5.

8. In neutral molecules, the algebraic sum of all the oxidation states is 0.

9. The highest positive oxidation state of the atoms of elements is determined by their group number. Exceptions are the elements of the copper subgroup (Cu, Ag, and Au), O, F, and also the metals of Group VIII. In the periods, the positive oxidation state grows across them (Fig. 23).

10. When writing equations of chemical reactions, one must always observe the rule that the algebraic sum of the oxidation states of all the atoms does not change. If in one component of a reaction the oxidation state

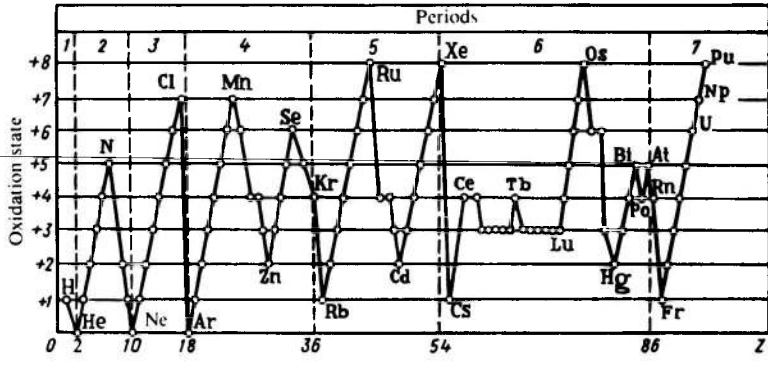


Fig. 23

Dependence of the highest positive oxidation state on the atomic number of an element

increases (an oxidation process), then the oxidation state of its partner in the reaction should decrease (a reduction process). This means that the oxidation and reduction processes are related and compensate each other.

When the oxidation state is indicated in a formula, it is written above the symbol of the relevant element with the appropriate sign, e.g. $\overset{+2}{Fe}$, $\overset{+6}{S}$, $\overset{+5}{Cl}$, and $\overset{-3}{N}$.

Examples of determining the oxidation state are given below:

P_4	P = 0	CH_4	C = −4,	H = +1
O_2	O = 0	CCl_4	C = +4,	Cl = −1
MnO_4^-	Mn = +7, O = −2	NH_4^+	N = −3,	H = +1
ClO_4^-	Cl = +7, O = −2			

When analysing the most important types of chemical reactions, we can say that some of them proceed with no change in the oxidation states of the atoms in the reactants (exchange reactions). Combination, decomposition, and replacement reactions proceed with a change in the oxidation states of the reactant atoms.

Reactions attended by the transfer of electrons from some atoms (or ions) to other atoms (or ions) as a result of which the oxidation state of the atoms (or ions) changes are called oxidation-reduction (redox) reactions.

Questions and Problems

1. What is the common feature of the oxidation state and valence and in what do they differ?
2. Can the oxidation state be considered a periodic function of the charge of the nucleus of atoms? Defend your answer using the periodic table of the elements.
3. Indicate the valence and oxidation state of each atom in the molecules Cl_2, H_2O, N_2, NH_3, and H_2S. Defend your answer using the theory of the structure of matter.
4. Determine the oxidation state of the atoms in the following compounds and ions: CrO_4^{2-}, Fe^{2+}, HNO_3, $KClO_3$, SO_4^{2-}, PO_4^{3-}, K_3PO_4, SiH_4, and NH_4^+.
5. Why is the concept "oxidation state" considered to be formal?
6. Why must one not take the real charge of an atom simultaneously as its oxidation state?

7.2. Oxidation and Reduction—Conjugate Processes. Oxidizing and Reducing Agents

Oxidation. If a neutral atom participates in a particular process, its loss of electrons raises its positive oxidation state. In the formed particle, the numerical value of the oxidation state equals the number of lost electrons:

$$\overset{0}{Na} - e^- \rightarrow \overset{+1}{Na} \qquad \overset{0}{Mg} + 2e^- \rightarrow \overset{+2}{Mg}$$

$$\overset{0}{Cl} - 5e^- \rightarrow \overset{+5}{Cl} \qquad \overset{0}{N} - 2e^- \rightarrow \overset{+2}{N}$$

When the molecules of simple substances are oxidized, account must be taken of the number of atoms in the molecule being oxidized and, accordingly, of the number of donated electrons:

$$\overset{0}{Cl_2} - 10e^- \rightarrow 2\overset{+5}{Cl} \qquad \overset{0}{N_2} - 4e^- \rightarrow 2\overset{+2}{N}$$

If atoms in the composition of a compound substance participate in an oxidation reaction, the loss of electrons by an atom increases its positive oxidation state by the number of units equal to the number of lost electrons:

$$\overset{+2}{N} - 3e^- \rightarrow \overset{+5}{N} \qquad \overset{+2}{Mn} - 5e^- \rightarrow \overset{+7}{Mn}$$

$$\overset{+3}{P} - 2e^- \rightarrow \overset{+5}{P} \qquad \overset{+2}{Pb} - 2e^- \rightarrow \overset{+4}{Pb}$$

$$\overset{-1}{Cl} - e^- \rightarrow \overset{0}{Cl} \qquad \overset{-3}{N} - 4e^- \rightarrow \overset{+1}{N}$$

$$2\overset{-1}{Cl} - 2e^- \rightarrow \overset{0}{Cl_2} \qquad \overset{-3}{N} - 8e^- \rightarrow \overset{+5}{N}$$

Reduction. If a neutral atom participates in a reduction process, the gaining of electrons causes the formation of negatively charged particles whose oxidation state numerically equals the number of gained electrons:

$$\overset{0}{Cl} + 2e^- \rightarrow 2\overset{-1}{Cl} \qquad \overset{0}{N_2} + 6e^- \rightarrow 2\overset{-3}{N}$$

$$\overset{0}{O_2} + 4e^- \rightarrow 2\overset{-2}{O} \qquad \overset{0}{P} + 3e^- \rightarrow \overset{-3}{P}$$

If positively charged particles participate in a reduction process, the gaining of electrons reduces the positive oxidation state by the number of units equal to the number of gained electrons:

$$\overset{+7}{Mn} + 5e^- \rightarrow \overset{+2}{Mn} \qquad \overset{+5}{Cl} + 2e^- \rightarrow \overset{+3}{Cl}$$

$$\overset{+6}{Cr} + 3e^- \rightarrow \overset{+3}{Cr} \qquad \overset{+6}{S} + 8e^- \rightarrow \overset{-2}{S}$$

Oxidation and reduction are two inseparable processes, hence they occur simultaneously and one cannot go on without the other one.

Let us consider the reaction of magnesium with chlorine:

$$Mg + Cl_2 = MgCl_2$$

Chlorine is more electronegative and gains the electrons donated by magnesium. Both processes can be depicted as follows:

$$\text{(reducing agent) } \overset{0}{Mg} - 2e^- \rightarrow \overset{+2}{Mg} \text{ (oxidation)}$$

$$\text{(oxidizing agent) } \overset{0}{Cl_2} + 2e^- \rightarrow 2\overset{-1}{Cl} \text{ (reduction)}$$

The magnesium loses two electrons, i.e. is oxidized, while the chlorine gains the two electrons and is reduced. In other words, the magnesium when becoming oxidized reduces the chlorine.

It thus follows that substances which donate electrons, i.e. are oxidized, are called **reducing agents**, while substances which gain electrons are **oxidizing agents**.

In the periodic table of elements, the reducing properties diminish across a period from the alkali metal to the noble gas, and the oxidizing properties grow. This is explained by the reduction in the atomic radii, the increase in the electron affinity and the growth in the electronegativity. It follows that the halogens and oxygen are the strongest oxidizing agents.

An oxidizing agent and the corresponding reducing agent are called a conjugate oxidation-reduction pair (or system).

In oxidation-reduction (redox) reactions, the oxidizing agent is reduced, and the reducing agent is oxidized.

Questions and Problems

1. Explain how the oxidation-reduction properties of the elements change in the periods and groups of the periodic table of elements.
2. How do the radii of neutral atoms affect their oxidizing properties?
3. Can data on the ionization energies be used to arrive at a conclusion on the oxidation-reduction properties of elements?
4. What is the relation between the electron affinity and the oxidation-reduction properties?
5. Which of the following processes are oxidation and which are reduction:

$$\overset{0}{Mg} \rightarrow \overset{+2}{Mg} \qquad \overset{+3}{Cr} \rightarrow \overset{+6}{Cr} \qquad \overset{+5}{N} \rightarrow \overset{+2}{N}$$

$$\overset{+2}{N} \rightarrow \overset{0}{N} \qquad \overset{+4}{Pb} \rightarrow \overset{+2}{Pb} \qquad \overset{-3}{N} \rightarrow \overset{+2}{N}$$

$$\overset{+3}{N} \rightarrow \overset{+5}{N} \qquad \overset{+3}{Fe} \rightarrow \overset{+2}{Fe} \qquad \overset{+7}{Mn} \rightarrow \overset{+2}{Mn}$$

$$\overset{-1}{Cl} \rightarrow \overset{0}{Cl} \qquad \overset{0}{Cu} \rightarrow \overset{+2}{Cu} \qquad \overset{+2}{Fe} \rightarrow \overset{0}{Fe}$$

Also indicate the number of donated or gained electrons.

6. Why are oxidation and reduction processes mutually related and mutually dependent?

7.3. Compiling Equations of Reactions

When compiling equations of oxidation-reduction reactions, two methods are customarily used, namely, the method of electron balance and the ion-electron (half-reaction) method.

Method of Electron Balance. The calculation of the gained and lost electrons is performed in accordance with the values of the oxidation states before and after a reaction. The equations of oxidation-reduction reactions are compiled in several steps.

1. A scheme of the reaction is written with indication of the oxidation states of the atoms of the elements participating in oxidation and reduction on the left and right sides:

$$\overset{+7}{K}\overset{+7}{Mn}O_4 + \overset{-1}{K}\overset{-1}{I} + H_2SO_4 \rightarrow K_2SO_4 + \overset{+2}{Mn}SO_4 + \overset{0}{I}_2 + H_2O$$

Here only manganese and iodine have changed their oxidation states.

2. The number of electrons gained or lost by the atoms or ions is determined:

$$\overset{+7}{Mn} + 5e^- \rightarrow \overset{+2}{Mn} \text{ (reduction)}$$

$$2\overset{-1}{I} - 2e^- \rightarrow I_2 \text{ (oxidation)}$$

3. The number of gained and donated electrons is balanced by introducing the necessary coefficients for the relevant reactants, using the smallest possible numbers:

$$\begin{array}{rl} \overset{+7}{Mn} + 5e^- \rightarrow \overset{+2}{Mn} & \mid 1 \\ \overset{-1}{I} - e^- \rightarrow \overset{0}{I} & \mid 5 \\ \hline \overset{+7}{Mn} + 5\overset{-1}{I} \rightarrow \overset{+2}{Mn} + 5\overset{0}{I} & \end{array}$$

The transition of $\overset{+7}{Mn}$ to $\overset{+2}{Mn}$ is attended by the gaining of five electrons, while the transition of $\overset{-1}{I}$ to $\overset{0}{I}$ by the loss of one electron. Therefore, five moles of $\overset{-1}{I}$ are needed for one mole of Mn(VII). The multipliers 1 obtained for Mn(VII) and Mn(II) and 5 for $\overset{-1}{I}$ and $\overset{0}{I}$ are the coefficients for the oxidizing agent $KMnO_4$ and the reducing agent KI, respectively. Since the reaction results in the formation of one mole of I_2, for which two moles of $\overset{-1}{I}$ are needed, the coefficients obtained must be doubled:

$$\begin{array}{rl} \overset{+7}{Mn} + 5e^- \rightarrow \overset{+2}{Mn} & \mid 2 \\ 2\overset{-1}{I} - 2e^- \rightarrow \overset{0}{I}_2 & \mid 5 \\ \hline 2\overset{+7}{Mn} + 10\overset{-1}{I} \rightarrow 2\overset{+2}{Mn} + 5\overset{0}{I}_2 & \end{array}$$

4. The found coefficients are inserted into the reaction equation before the corresponding formulas of the substances on the left and right sides.

The coefficients are calculated for sulphuric acid (on the left side), potassium sulphate and water (on the right side) by comparing the number of atoms or ions on both sides of the scheme.

Proceeding from the electron balance, we insert the obtained coefficients before the relevant components:

$$2KMnO_4 + 10KI + H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5I_2 + H_2O$$

The number of potassium ions on the left side is 12, and on the right side it is 2. Therefore on the right side we add the coefficient 6 before K_2SO_4:

$$2KMnO_4 + 10KI + H_2SO_4 \rightarrow 2MnSO_4 + 5I_2 + 6K_2SO_4 + H_2O$$

On the right side, the number of sulphate ions is 8 ($6K_2SO_4$ and $2MnSO_4$), hence eight moles of sulphuric acid must enter into the reaction. We put the coefficient 8 before sulphuric acid on the left side. Since the number of hydrogen atoms on the left side is now 16, the coefficient 8 will do for water. The final molecular equation is:

$$2KMnO_4 + 10KI + 8H_2SO_4 = 2MnSO_4 + 5I_2 + 6K_2SO_4 + 8H_2O$$

Hence, $KMnO_4$ is the oxidizing agent and KI is the reducing agent.

Sometimes the above method of taking into account the complete change in the oxidation states does not enable one to correctly compile reaction equations in which one of the substances participating in the reaction simultaneously performs two functions—of an oxidizing agent (or a reducing agent) and a salt-forming agent. Let us consider as an example the reaction

$$\overset{0}{Mg} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Mg}(\overset{+5}{N}O_3)_2 + \overset{+1}{N}_2O + H_2O$$

Magnesium loses two electrons, while nitrogen $\overset{+5}{N}$ gains four electrons:

$$\begin{array}{r|l} \overset{0}{Mg} - 2e^- \rightarrow \overset{+2}{Mg} & 4 \\ \overset{+5}{2N} + 8e^- \rightarrow \overset{+1}{2N} & 1 \end{array}$$

$$4\overset{0}{Mg} + \overset{+5}{2N} = 4\overset{+2}{Mg} + \overset{+1}{2N}$$

But this alone does not allow us to compile the equation of the reaction correctly. The explanation is that in addition to the function of an oxidizing agent, the nitric acid also binds the magnesium ions in the form of a nitrate without changing the oxidation state of the nitrogen $\overset{+5}{N}$. Therefore the coefficient before HNO_3 in the reaction equation must take into account both functions of the nitric acid—an oxidizing agent and a salt-forming one.

To oxidize four moles of magnesium atoms, two moles of HNO_3 are needed, and above this amount eight moles of HNO_3 to bind four ions Mg^{2+}:

$$4Mg + \underset{\text{(for oxidizing)}}{2HNO_3} + \underset{\text{(for binding)}}{8HNO_3} = 4Mg(NO_3)_2 + N_2O + 5H_2O$$

The result is:

$$4Mg + 10HNO_3 = 4Mg(NO_3)_2 + N_2O + 5H_2O$$

Reactions are encountered in which the number of particles changing their oxidation state exceeds two. Here the total number of electrons donated by the reducing agents and the total number of them gained by the oxidizing agents are calculated; otherwise the rules described above remain in force:

$$\overset{+3}{As_2}\overset{-2}{S_3} + 28\overset{+5}{HNO_3} + 4H_2O = 6H_3\overset{+5}{AsO_4} + 9H_2\overset{+6}{SO_4} + 28\overset{+2}{NO}$$

$$\left.\begin{array}{l} \overset{+3}{2As} - 4e^- \rightarrow \overset{+5}{2As} \\ \overset{-2}{3S} - 24e^- \rightarrow \overset{+6}{3S} \end{array}\right\} 28e^- \quad \Big| \; 3$$

$$\overset{+5}{N} + 3e^- \rightarrow \overset{+2}{N} \qquad\qquad \Big| \; 28$$

$$\overset{+3}{6As} + \overset{-2}{9S} + 28\overset{+5}{N} = 6\overset{+5}{As} + 9\overset{+6}{S} + 28\overset{+2}{N}$$

The Ion-Electron (Half-Reaction) Method. By this method, oxidation and reduction are considered as independent processes, each of which reflects a half of the entire reaction equation. Hence comes the name "half-reaction".

For instance, the following reaction proceeding in a solution:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

$$2Fe^{3+} + 6Cl^- + Sn^{2+} + 2Cl^- = 2Fe^{2+} + 4Cl^- + Sn^{4+} + 4Cl^-$$

can be represented as a set of two processes:

oxidation of the Sn^{2+} ion to Sn^{4+}:

$$Sn^{2+} - 2e^- \rightarrow Sn^{4+}$$

reduction of the Fe^{3+} ion to Fe^{2+}:

$$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$$

To compile the equation of an oxidation-reduction reaction by the ion-electron (half-reaction) method, one must observe the following rules.

1. In the compounds participating in the oxidation-reduction reaction, the charges of the ions are determined instead of the oxidation state of the relevant atoms:

$$KMnO_4 + KI + H_2SO_4 \rightarrow MnSO_4 + I_2 + K_2SO_4 + H_2O$$

or in the ionic form:

$$K^+ + MnO_4^- + K^+ + I^- + 2H^+ + SO_4^{2-} \rightarrow$$
$$\rightarrow Mn^{2+} + SO_4^{2-} + I_2 + 2K^+ + SO_4^{2-} + H_2O$$

2. An ionic scheme of the reaction is compiled after determining the oxidizing and reducing agents. Only the ions actually participating in oxidation and reduction are indicated:

$$MnO_4^- + I^- + H^+ \rightarrow Mn^{2+} + \overset{0}{I} + H_2O$$

We see that the ions MnO_4^- are reduced to Mn^{2+} and I^- is oxidized to $\overset{0}{I}$.

The participation of a hydrogen ion in the reaction indicates that the process occurs in an acidic solution. This is very important for our further reasoning.

3. Ion-electron equations are compiled for each half-reaction. It must be taken into account that if the reactants contain more oxygen atoms than the products, as many H^+ ions are added to the left side of the half-reaction as are needed for bonding the required number of oxygen atoms (this can be done because the solution is acidic). The corresponding number of water molecules is added to the right side of the half-reaction:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

The number of electrons indicated in each half-reaction must equal the total change in the charges of the ions in the relevant process. The second half-reaction is $2I^- - 2e^- \rightarrow \overset{0}{I}_2$.

4. The equation of each half-reaction is multiplied by the smallest possible multiplier making the number of electrons in the reduction process equal to that in the oxidation process. After this, the equations of the two half-reactions are summated by terms and a balanced equation of the complete reaction is obtained:

$2I^- - 2e^- \rightarrow \overset{0}{I}_2$	5 (oxidation)
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	2 (reduction)

$$10I^- + 2MnO_4^- + 16H^+ = 5I_2 + 2Mn^{2+} + 8H_2O$$

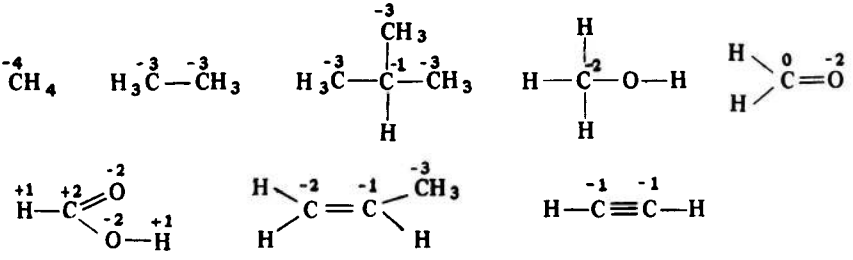
5. The obtained coefficients are written in the main equation before the relevant substances:

$$2KMnO_4 + 10KI + 8H_2SO_4 = 2MnSO_4 + 5I_2 + 6K_2SO_4 + 8H_2O$$

If the solution is acidic, the number of oxygen atoms can also be balanced by water molecules.

In the equations of reactions proceeding in an alkaline solution, the number of oxygen atoms in the half-reactions is balanced either by OH^- ions or water molecules, and in a neutral solution only by water molecules.

Oxidation-reduction reactions with the participation of organic substances cause definite difficulties. This is associated with finding the oxidation state of the carbon atoms in such molecules. Let us consider examples:



In the reaction of ethylene hydrogenation, the oxidation state of carbon changes from -2 to -3 (in ethane):

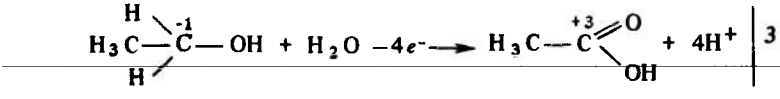
$$H_2\overset{-2}{C}=\overset{-2}{C}H_2 + H_2 \rightarrow H_3\overset{-3}{C} - \overset{-3}{C}H_3$$

The oxidation of ethanol by potassium dichromate proceeds by the equation

$$3\overset{-3}{C}H_3-\overset{-1}{C}H_2OH + 2Na_2\overset{+6}{C}r_2O_7 + 8H_2SO_4 \rightarrow$$

$$\rightarrow 3CH_3-\overset{+3}{C}(=O)-OH + 2Cr_2(SO_4)_3 + Na_2SO_4 + 11H_2O$$

(a) the half-reaction of ethanol oxidation is:



(b) the half-reaction of dichromate reduction is:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \mid 2$$

$$3CH_3CH_2OH + 3H_2O - 12e^- + 2Cr_2O_7^{2-} + 28H^+ + 12e^- \rightarrow$$
$$\rightarrow 3CH_3COOH + 4Cr^{3+} + 12H^+ + 14H_2O$$
$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

Questions and Problems

1. Iron(III) chloride exhibits oxidizing properties, and Fe^{3+} transforms into Fe^{2+}. Compile the equation of the reaction of iron(III) chloride with potassium iodide.

2. Determine the oxidizing and reducing agents and find the coefficients in the unbalanced equations of the following reactions:

(a) $KMnO_4 + NH_3 \rightarrow KNO_3 + MnO_2 + KOH + H_2O$

(b) $K_2Cr_2O_7 + HClO_4 + HI \rightarrow Cr(ClO_4)_3 + KClO_4 + I_2 + H_2O$

(c) $KClO_3 + HCl \rightarrow Cl_2 + KCl + H_2O$

(d) $I_2 + H_2O + Cl_2 \rightarrow HIO_3 + HCl$

3. Using the half-reaction method, find the coefficients in the following unbalanced reaction equations:

(a) $K_2Cr_2O_7 + K_2SO_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + H_2O$

(b) $PbO_2 + MnSO_4 + HNO_3 \rightarrow PbSO_4\downarrow + HMnO_4 + Pb(NO_3)_2 + H_2O$

7.4. Types of Reactions

Three types of oxidation-reduction reactions are distinguished.

Intermolecular reactions are ones proceeding with a change in the oxidation state of the atoms in different molecules. This type of reactions is the most widespread.

Intramolecular reactions are ones attended by a change in the oxidation state of different atoms in one molecule. This mechanism is observed most frequently in reactions of the thermal decomposition of molecules, for instance:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

$$2KClO_3 = 2KCl + 3O_2$$

$$NH_3NO_3 = N_2O + 2H_2O$$

Disproportionation reactions (auto oxidation-reduction) in which the oxidation state of atoms of the same element simultaneously changes in both directions. An essential condition for such oxidation-reduction reactions is the presence in a molecule of an atom having an oxidation state intermediate between its minimal and maximal ones. An example of such reactions is:

$$2\overset{0}{Cl_2} + 6KOH = 5K\overset{-1}{Cl} + K\overset{+5}{Cl}O_3 + 3H_2O$$

How a substance will behave in a given reaction (as an oxidizing or reducing agent) depends chiefly on the medium whose influence can change the nature of an oxidation-reduction reaction between the same reactants.

We can use $KMnO_4$ as an example to illustrate reactions in which the degree of reduction of $\overset{+7}{Mn}$ depends on the reaction of the solution. If we

pour a solution of K_2SO_3 into a solution of $KMnO_4$ containing sulphuric acid, the reaction mixture rapidly loses its colour and the $\overset{+7}{Mn}$ is reduced to $\overset{+2}{Mn}$:

$$2KMnO_4 + 5K_2SO_3 + 3H_2SO_4 = 2MnSO_4 + 6K_2SO_4 + 3H_2O$$

If $KMnO_4$ reacts with K_2SO_3 in a neutral solution, the $\overset{+7}{Mn}$ is reduced to $\overset{+4}{Mn}$, and the solution acquires an alkaline reaction:

$$2KMnO_4 + 3K_2SO_3 + H_2O = 2MnO_2 + 3K_2SO_4 + 2KOH$$

In an alkaline solution, manganate ions form:

$$2KMnO_4 + K_2SO_3 + 2KOH = 2K_2MnO_4 + K_2SO_4 + H_2O$$

Questions and Problems

1. Which of the following reactions belong to intramolecular ones and which belong to disproportionation ones:

(a) $KClO_3 \rightarrow KClO_4 + KCl$

(b) $KClO_3 \rightarrow KCl + O_2$

(c) $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + H_2O$

(d) $Cu(NO_3)_2 \rightarrow CuO + NO_2 + O_2$

(e) $Na_2SO_3 \rightarrow Na_2SO_4 + Na_2S$

Balance the equation for each reaction by the electron-balance method.

2*. Through a potassium iodide solution there were passed 100 ml of a mixture containing chlorine. Iodine crystallized out in an amount of 0.381 g. Is the given process an oxidation-reduction one? Determine the composition of the gas mixture in per cent by volume.

3. The products of roasting barium nitrate include barium oxide and a nitrogen-containing gas, as well as a substance contained in the air. Write the equation of the reaction and indicate the oxidizing and reducing agents.

4*. Tin(II) chloride can be obtained by reacting metallic tin with a 30% HCl solution. Hydrogen is evolved in the reaction. Compile the equation of the oxidation-reduction reaction, and also calculate the volume of hydrogen evolved in the "dissolving" of 40 g of tin.

5*. Aluminium reacts with concentrated alkalies by the unbalanced equation

$$Al + NaOH + H_2O = NaAlO_2 + H_2$$

Compile the electron balance equation, choose the coefficients, and calculate the mass of aluminium needed to obtain 6.72 lit of H_2.

6*. Nitric acid is a strong oxidizing agent and oxidizes many non-metals. For instance, it reacts with iodine as follows:

$$I_2 + HNO_3 \rightarrow HIO_3 + NO + H_2O$$

Balance the reaction equation and calculate the mass of the reacted iodine if 2.8 lit of nitrogen(II) oxide evolved.

7.5. Electrolysis

Oxidation-reduction reactions can also proceed under the effect of an electric current.

Most electrolytes, as already mentioned, are conductors of an electric current in aqueous solutions, while some of them (salts and bases) also conduct electricity in the molten state.

The following phenomena are observed when a direct current is passed through an electrolyte solution or melt: the positively charged ions—cations—approach the negative electrode—cathode, and the negatively charged ions—anions—approach the positive electrode—anode. The current passes through the solution (or melt) because of the migration of the ions in the solution (or melt); electrons from the anions pass over onto the anode, and electrons from the cathode pass over to the cations (Fig. 24).

Consequently, oxidation takes place on the anode because electrons are given up to it, and reduction takes place on the cathode because electrons are attached to the ions.

Chemical reactions proceeding under the effect of an electric current on electrodes placed in a solution, melt, or solid electrolyte are called electrolysis.

Two types of anode electrodes can be used in electrolysis, namely, active (consumable) and inert (non-consumable) ones. An active anode becomes oxidized and passes into the solution in the form of ions, whereas an inert anode is only an electrode via which electrons are transmitted into the solution (or melt). Inert electrodes are generally made from graphite or platinum.

Let us consider the electrolysis of a molten salt—sodium chloride (graphite electrodes). When a current is passed through the system, three processes occur simultaneously:

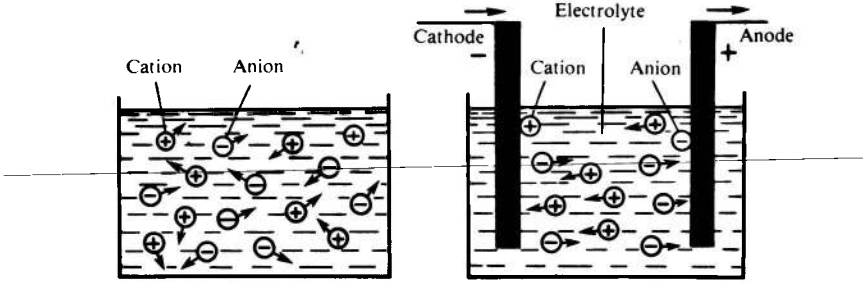


Fig. 24

Mechanism of the passage of an electric current through an electrolyte solution: *a*—chaotic motion of the ions in the electrolyte without an electric field; *b*—directed motion of the ions in the solution in a constant electric field

(1) migration of the cations Na^+ toward the cathode and of the Cl^- anions toward the anode;

(2) oxidation of the chloride ion Cl^- on the anode:

$$Cl^- - e^- \rightarrow \frac{1}{2}Cl_2$$

(3) reduction of the Na^+ ion on the cathode:

$$Na^+ + e^- \rightarrow Na$$

The overall electrolysis of a melt of NaCl is described by the equation:

$$Na^+ + Cl^- \xrightarrow{\text{electrolysis}} \overset{\circ}{Na} + \frac{1}{2}\overset{\circ}{Cl}_2$$

or

$$2NaCl \xrightarrow{\text{electrolysis}} 2Na + Cl_2$$

The electrolysis of dilute aqueous solutions of salts is a much more involved process because of the presence of water. Competition of the ions occurs because the water ions can participate in electrolysis. Here three processes occur simultaneously, but they may go on differently:

(1) directed migration of the ions (Na^+ toward the cathode and Cl^- toward the anode);

(2) oxidation on the anode:

$$Cl^- - e^- \rightarrow \frac{1}{2}Cl_2$$

in very dilute solutions, the following oxidation reaction is possible:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

(3) reduction on the cathode:

$$Na^+ + e^- \rightarrow Na$$

or

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

If two or more reactions can proceed on the same electrode, the one requiring a lower e.m.f. (electromotive force) has superiority.

To determine this, it is necessary to use for cations the electrochemical or electromotive series of the metals (in which the latter are arranged in the order of the growth in their oxidizing activity). The closer a metal is to the beginning of the series, the more difficult is it to reduce an ion of the metal (the latter accepts electrons with greater difficulty). This also relates to hydrogen.

Anions can also be arranged in a series in accordance with the growth

in their reducing activity:

$$F^-,\ NO_3^-,\ SO_4^{2-},\ OH^-,\ Cl^-,\ Br^-,\ I^-,\ S^{2-}$$

Consequently, in the electrolysis of an aqueous solution of NaCl, the discharge of the ions of the water itself, in particular H^+, occurs more easily than discharge of the Na^+ ion. For this reason in the electrolysis of an aqueous solution of NaCl, the chloride ions Cl^- discharge on the anode and Cl_2 evolves, while hydrogen ions H^+ discharge on the cathode and H_2 evolves. The Na^+ ions do not discharge. The OH^- and Na^+ ions accumulate in the solution, which can be seen from the overall equation:

$$2H_2O + 2Cl^- \rightarrow Cl_2 + H_2 + 2OH^-$$

or

$$2H_2O + 2NaCl \xrightarrow{\text{electrolysis}} Cl_2 + H_2 + 2NaOH$$

Hence, sodium hydroxide forms in the solution.

If a salt is formed by an active metal and an oxyacid, then the electrolysis of the salt leads to the formation of hydrogen on the cathode and oxygen on the anode.

On the cathode:

$$2HOH + 2e^- \rightarrow H_2 + 2OH^-$$

Two electrons from the cathode react with two molecules of water to form a molecule of hydrogen and two hydroxyl ions.

On the anode:

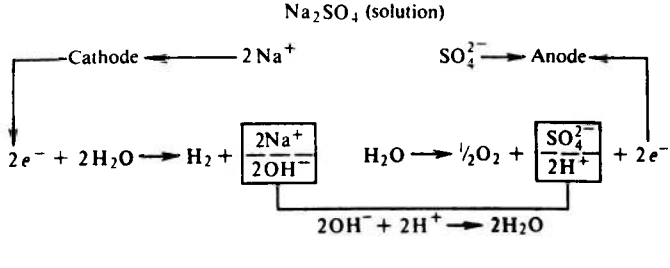
$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

Summation of these two reactions yields:

$$2HOH + 2e^- + HOH \rightarrow H_2 + 2OH^- + \frac{1}{2}O_2 + 2H^+ + 2e^-$$

$$3H_2O \xrightarrow{\text{electrolysis}} H_2 + \frac{1}{2}O_2 + 2H_2O$$

The water formed by reaction of the H^+ and OH^- ions (with each other again) is shown on the right side in the overall equation. A diagram of the described electrolysis process is shown below:



The following reactions proceed in the electrolysis of a concentrated HCl solution (platinum electrodes):

on the cathode: $2H^+ + 2e^- \rightarrow H_2$

on the anode: $2Cl^- - 2e^- \rightarrow Cl_2$

The formed hydrogen and chlorine evolve from the solution.

In the electrolysis of an aqueous $CuCl_2$ solution (carbon or platinum electrodes), the following reactions proceed on the electrodes:

on the cathode:

$$Cu^{2+} + 2e^- \rightarrow \overset{0}{Cu}$$

on the anode

$$2Cl^- - 2e^- \rightarrow \overset{0}{Cl_2}$$

the overall reaction is:

$$Cu^{2+} + 2Cl^- \rightarrow \overset{0}{Cu} + \overset{0}{Cl_2}$$

Metallic copper is deposited on the cathode, and gaseous chlorine evolves at the anode.

Questions and Problems

1. What is the difference between the electrolysis of melts and solutions of salts?
2. Consider the electrolysis of a melt and solution of potassium chloride, magnesium sulphate, and silver nitrate.

7.6. The Electromotive Series of Metals

When any metal is immersed in an electrolyte solution, a potential difference known as the **electrode potential** appears at the metal-solution interface. The causes of the appearance of this potential may vary. For example, when a zinc plate is immersed in water or a zinc salt solution, the polar molecules of water act with their negative poles on the positive ions of the metal crystal lattice, "extract" them and transfer them into the solution. Electrons remain on the metal surface and charge it negatively. The hydrated metal ions that have passed into the solution are attracted by the charged surface of the plate and take up a position near it. The result is the formation of two layers with opposite charges, what is called an **electrical double layer**. It can be likened to a plane microcapacitor in which the metal surface is the negative plate and the metal ions in the solution are the positive one (Fig. 25).

The transition of metal ions into a solution is a reversible process.

If a plate is made from a metal with a low activity such as copper, then when it is immersed in a copper salt solution the reverse process will

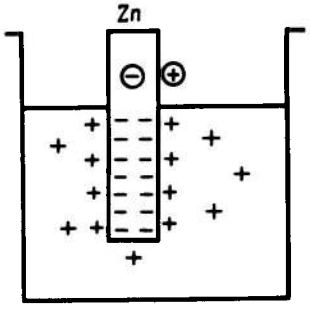


Fig. 25
Appearance of an electrical double layer on a zinc plate immersed in a solution

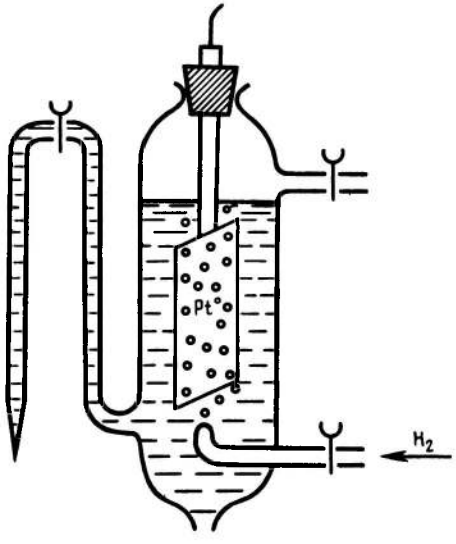


Fig. 26
A hydrogen electrode

predominate, namely, the metal ions will lose their hydrate shell and pass from the solution into the crystal lattice of the metal, charging the plate positively. The solution, on the other hand, is charged negatively owing to the excess of anions remaining in it. The result is again the appearance of an electrical double layer and, consequently, a definite electrode potential.

Therefore, when metals are immersed in solutions of their salts, some of them (the less active ones) are charged positively, while others (the more active ones), conversely, are charged negatively. The potential of each metal depends on its nature, the concentration of its ions in the solution, and the temperature.

It is impossible to directly measure the potential of an individual electrode. This is why the electrode potentials are measured by comparing them with the potential of an electrode taken as a standard or reference one. Generally, the **standard hydrogen electrode** is used for this purpose, and its potential is conditionally taken as zero. This electrode consists of a platinum plate coated with platinum black (electrolytically deposited platinum) immersed in a sulphuric acid solution (c = 1 mol/lit). A stream of gaseous hydrogen under a pressure of 101.325 kPa flows around the electrode (Fig. 26).

If a plate of any metal immersed in a solution of its salt containing one mole of ions of the metal in 1000 g of water is connected to a hydrogen electrode, a galvanic cell is obtained whose e.m.f. is easy to measure. It is exactly this e.m.f. measured at 25 °C that is called the **standard electrode potential** $E°$ of the given metal.

By arranging metals in the order of the increasing algebraic values of their standard electrode potentials $E°$, we obtain a series called the **electrochemical** or **electromotive series of the metals:**

Increase in reducing ability ←

Li	Cs	K	Ca	Na	Mg	Al	Mn	Zn	Cr
−3.04	−3.01	−2.92	−2.87	−2.71	−2.37	−1.66	−1.18	−0.76	−0.74
Li^+	Cs^+	K^+	Ca^{2+}	Na^+	Mg^{2+}	Al^{3+}	Mn^{2+}	Zn^{2+}	Cr^{3+}

Fe	Ni	Sn	Pb	H_2	Cu	Ag	Hg	Au
−0.44	−0.25	−0.14	−0.13	−0.00	+0.34	+0.80	+0.85	+1.50
Fe^{2+}	Ni^{2+}	Sn^{2+}	Pb^{2+}	$2H^+$	Cu^{2+}	Ag^+	Hg^{2+}	Au^{3+}

Increase in oxidizing ability →

This series characterizes the chemical properties of the metals.

When the algebraic value of the potential is lower, the reducing ability of the metal is higher and the oxidizing ability of its ions is lower. Inspection of the series reveals that metallic lithium is the strongest reducing agent, and gold is the weakest one. Conversely, the gold ion Au^{3+} is the strongest oxidizing agent, and the lithium ion Li^+ is the weakest one.

In the electromotive series, each preceding metal displaces the following one from a solution of its salts.

Questions and Problems

1. What is the relation between the electromotive series and electrolysis?
2. How does the position of the metals in the electromotive series agree with their position in the periodic table of the elements?
3. What is the relation between the ionization energy of metals and their position in the electrochemical series?
4. Give examples of reactions that can be explained using the electromotive series of the metals.

SUMMARY

The reaction of substances with one another is attended by the transfer of electrons from one set of reactants to another. Such processes are called oxidation-reduction ones. The transfer of electrons results in a change in the oxidation state of the particles participating in the process. With respect

to the concept of the oxidation state, it is conditionally assumed that a molecule consists only of ions.

Any oxidation-reduction process is a combination of two inseparably related and mutually caused processes—oxidation and reduction.

The equations of oxidation-reduction reactions are compiled by the electron balance or ion-electron (half-reaction) method. In the former, the number of lost and gained electrons is counted in accordance with the values of the oxidation states (numbers) before and after a reaction. The second method is based on the compiling of a net ionic equation with the inclusion of only the ions participating in the oxidation and reduction processes.

Oxidation-reduction reactions proceeding on electrodes in solutions or melts of electrolytes when an electric current is passed through them form the process known as electrolysis. The participation of metals in reactions with the transfer of electrons is determined by their position in the electromotive series.

Part II

INORGANIC CHEMISTRY

CHAPTER 8

HYDROGEN. WATER

OBJECTIVES

To have a comprehensive notion of hydrogen as a chemical element and simple substance, and also of water as the most widespread and important hydrogen compound from the viewpoints of the studied theories.

8.1. Hydrogen

Its chemical symbol is H. Its atomic number is 1 and atomic mass is 1.007 97. The number of known isotopes is four, of which $^{1}_{1}H$—protium, $^{2}_{1}H$—deuterium (its symbol is D), and $^{3}_{1}H$—tritium (symbol T) have been discovered in nature, while the fourth isotope $^{4}_{1}H$ has been obtained artificially. The nucleus of a hydrogen atom contains one proton. The electron configuration of hydrogen is $1s^1$. The main distinction of hydrogen from the other elements is that its only electron is directly in the sphere of action of the atomic nucleus—it has no intermediate electron layer. When hydrogen loses an electron, the positive ion H^+ forms, which is an elementary particle—a proton.

The content of hydrogen in the Earth's crust is 1%. It occurs in nature both in the free state (volcanic gases, the gases of petroleum wells, the upper layers of the atmosphere) and in the form of compounds. The most widespread of the latter is water, where the content of hydrogen is 11.11% (by mass).

The question of hydrogen's place in the periodic table of the elements acquires special significance from modern standpoints. The electron structure of hydrogen's single shell is similar to the outer shell of the alkali metals. Like the latter, hydrogen has the highest oxidation state of +1 of the singly charged ion H^+. These basic factors allow hydrogen to be considered as a representative of Group I, but they are all formal to a sufficient extent. For example, the ionization energy of a hydrogen atom is much greater than that of the alkali metal atoms. Another important distinction must also be noted, namely, the existence of negatively charged ions is impossible

for the alkali metals, whereas the oxidation state of -1 is encountered in hydrogen (for example, $\overset{+1}{Na}\overset{-1}{H}$). The radius of an H^+ ion is incomparably smaller than the radii of the alkali metal ions, while the latter, as is general knowledge, have the largest radii of all other positive ions. Hence, there is only a certain formal similarity between hydrogen and the alkali metals.

On the other hand, hydrogen is included in Subgroup VIIA. Is this justified from the viewpoint of electron structure?

Hydrogen lacks one electron up to filling in the outer shell to that of the noble gas helium. The same is observed in a halogen, in which there is also one electron less than in the outer shell of the relevant noble gas. In its compounds with metals, hydrogen, like the halogens, forms the negative ion H^- ($\overset{+}{Na}\overset{-}{H}$ and $\overset{+}{Na}\overset{-}{Cl}$). In their nature, these compounds remind one of typical salts similar to the relevant compounds of fluorine or chlorine. Hydrogen, like the halogens, is characterized by a high value of the ionization energy. It is just these features that allow us to place hydrogen in the halogen subgroup.

In accordance with the structure of the periodic table, the charges of the nuclei of analogous elements in the small periods should differ from one another by eight units. Therefore, hydrogen as the element with the atomic number 1 can be considered as an analogue of fluorine (atomic number 9), and not of lithium, whose atomic number is 3. But it must always be remembered that this analogy is nevertheless relative.

When discussing whether to place hydrogen in Group I or Group VII, preference is given to Group VII with a view to the structure of the outer (and only) electron layer lacking one electron to its completion, the value of the ionization energy, the possibility of a negative oxidation state, and the small atomic radius.

Questions and Problems

1. Draw up a plan of the characteristics of hydrogen as a chemical element.
2. Can we say that the atomic nucleus of any hydrogen isotope transforms into a proton when it loses an electron?
3. Describe the process of formation and structure of a hydride ion.

8.2. Ways of Preparing Hydrogen

At a laboratory, hydrogen is most often prepared by reducing metals to the left of it in the electromotive series from water or acids:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow, \qquad \Delta H < 0$$

$$2Na + 2HOH = 2NaOH + H_2\uparrow, \qquad \Delta H < 0$$

Hydrogen is produced commercially by:

1. The conversion of methane. The process consists in reacting methane with steam at 800-900 °C:

$$CH_4 + H_2O = CO\uparrow + 3H_2\uparrow, \qquad \Delta H > 0$$

The mixture of gases is further separated into its components by cooling.

2. The deep cooling of coke gas. Three fractions form when coking coal: a solid one—coke, a liquid one—coal tar, and a gaseous one containing hydrogen (up to 60% by volume) in addition to hydrocarbons. This fraction after special chemical treatment is subjected to deep cooling for separating the hydrogen from the other substances in this fraction.

3. The electrolysis of water:

$$2H_2O \xrightarrow{\text{electrolysis}} 2H_2 + O_2$$

4. The iron-steam method. The process consists in oxidizing red-hot iron by steam. Different iron oxides form depending on the temperature conditions:

$$Fe + HOH = FeO + H_2\uparrow, \qquad \Delta H > 0$$
$$3Fe + 4HOH = Fe_3O_4 + 4H_2\uparrow, \qquad \Delta H > 0$$

An advantage of this method consists in that the iron is further reduced by the water gas and is again used in the reaction, which ensures continuity of the process.

5. The conversion of carbon. First water gas is produced by passing steam through red-hot coke at 1000 °C:

$$C + H_2O = CO\uparrow + H_2\uparrow, \qquad \Delta H > 0$$

it is then mixed with steam and passed over the catalyst Fe_2O_3 heated to 400-450 °C. The carbon(II) oxide reacts with the steam:

$$CO + H_2O + (H_2) = CO_2 + 2H_2\uparrow, \qquad \Delta H > 0$$

Questions and Problems

1. Consider each hydrogen production reaction from the viewpoint of oxidation and reduction. Indicate the oxidizing and reducing agents.

2. Can hydrogen be produced by reacting: (a) zinc with sulphuric acid; (b) magnesium with hydrochloric acid; (c) iron with hydrochloric acid; (d) calcium with water; (e) calcium with sulphuric acid; and (f) zinc with nitric acid? Compile equations of the oxidation-reduction reactions for all possible cases.

3[a]. What volume of hydrogen can be obtained when hydrochloric acid is reacted with 10 g of an iron-zinc alloy if the percentage by mass of the zinc in the alloy is 60%?

8.3. Properties of Hydrogen

Physical Properties. Hydrogen is a colourless, tasteless, and odourless gas. It is the lightest of all gases: one litre has a mass of 0.09 g; it is 14.4 times lighter than air; its density at standard temperature and pressure (STP) is 0.0899 g/lit. Its boiling (liquefaction) point is -252.6 °C, and its melting point is -259.1 °C.

Hydrogen dissolves very sparingly in water (2 ml of hydrogen in 100 ml of water); it is featured by a solubility in metals, which is explained by its ability to diffuse through metal walls.

Chemical Properties. Hydrogen can participate in three types of electron processes.

When an electron is lost, a proton H^+ forms. In aqueous solutions, the H^+ ion combines with a water molecule to form a hydroxonium (hydronium) ion H_3O^+.

The gaining of an electron leads to the formation of the hydride ion H^- whose electron configuration $1s^2$ corresponds to the helium shell. The hydride ion exists only in crystalline hydrides of the most electropositive metals (NaH, CaH_2).

The formation of electron-pair (covalent) bonds occurs when molecules of hydrogen form and when hydrogen reacts with non-metals. A hydrogen molecule consists of two atoms joined by a strong covalent bond (the dissociation energy of this bond is 436 kJ/mol).

The H_2 molecules decompose into atoms at a temperature above 2000 °C. This explains the rather low chemical activity of hydrogen at standard temperature and pressure. Hydrogen does not react with oxygen at STP, but when the mixture is ignited, they react with an explosion:

$$2H_2 + O_2 = 2H_2O$$

A mixture of two volumes of hydrogen and one volume of oxygen is called **detonating gas.**

Hydrogen reacts differently with the halogens. Its reaction with fluorine at any temperature proceeds with an explosion:

$$H_2 + F_2 = 2HF$$

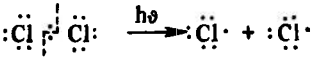
With chlorine, an explosion occurs in the light:

$$H_2 + Cl_2 = 2HCl$$

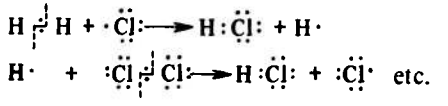
The reaction with bromine proceeds less vigorously, while with iodine it does not proceed to the end even at a high temperature.

The reaction of hydrogen with chlorine is of considerable interest from the viewpoint of its mechanism. In the dark, hydrogen and chlorine do

not react at room temperature, and with slight illumination the rate of the reaction is insignificant. With strong illumination, the reaction proceeds instantaneously with an explosion. Studying of the mechanism of this process has shown that it consists of consecutive elementary substitution reactions. Light causes a chlorine molecule to decompose into two atoms:



The formed atoms further induce a chain of elementary reactions: the atomic chlorine attacks a hydrogen molecule, which results in the formation of hydrogen chloride and atomic hydrogen:



Processes of this kind are called **chain reactions.**

When hydrogen is passed through molten sulphur, hydrogen sulphide forms:

$$H_2 + S = H_2S$$

Its reaction with nitrogen is reversible:

$$3H_2 + N_2 \rightleftarrows 2NH_3, \qquad \Delta H < 0$$

Hydrogen forms hydrides with the alkali and alkaline-earth metals:

$$2Na + H_2 = 2NaH$$
$$2Li + H_2 = 2LiH$$
$$Ca + H_2 = CaH_2$$

In these reactions, hydrogen is a typical oxidizing agent. When it gains an electron, a hydrogen atom transforms into a hydride ion whose electron shell has the configuration $1s^2$ (as in helium):

$$Ca - 2e^- = Ca^{2+} \quad \text{(reducing agent)}$$
$$H_2 + 2e^- = 2H^- \quad \text{(oxidizing agent)}$$

The compounds of hydrogen with metals (hydrides) are typical ionic ones and are characterized by strong reducing properties. Already in the presence of traces of water they decompose into the relevant hydroxide and hydrogen, e.g.:

$$NaH + HOH = NaOH + H_2$$

Hydrogen reduces many metals from their oxides:

$$CuO + H_2 = Cu + H_2O$$

This reaction is used to produce some metals.

Hence, apart from reaction with metals, **hydrogen exhibits reducing properties.**

Application. Hydrogen is widely used in various branches of industry: in the production of aniline dyes, in the synthesis of hydrogen chloride, ammonia (the latter is further used to produce nitrogen fertilizers), and in the reduction of some non-ferrous metals from their ores. In the food industry, hydrogen is widely used in the production of substitutes for animal fats (margarines).

Questions and Problems

1. What are the valence and oxidation state of hydrogen in the composition of a simple substance?

2. Prove that in reactions with non-metals hydrogen behaves like a reducing agent, and with metals like an oxidizing agent.

3. Why is the rate of the reaction between hydrogen and oxygen at STP practically equal to zero? Defend your answer from the viewpoint of the structure of H_2 and O_2 molecules.

4. Atomic hydrogen is a more vigorous reducing agent than molecular hydrogen. Why?

5. Why does the hydride ion have reducing properties? Confirm this using the example of the reaction of CaH_2 with water.

6. Why is the reaction $CuO + H_2 = Cu + H_2O$ possible, while the reverse process is impossible? Explain your answer.

7[a]. How many litres of hydrogen are needed to reduce 24 g of copper(II) oxide?

8[a]. When treating 8.93 g of lead(II) oxide with hydrogen, 0.54 g of water formed. How many grammes of the oxide were reduced? What was the mass of the residue?

9[a]. When treating a specimen consisting of a mixture of zinc and iron with hydrochloric acid, 0.896 lit of hydrogen evolved, while when an identical specimen was treated with an alkali solution, 0.448 lit of hydrogen evolved. Determine the composition of the mixture in per cent.

10[a]. What volume of hydrogen will evolve when 10 g of a mixture of aluminium and aluminium oxide is reacted with hydrochloric acid if the content of Al_2O_3 in the mixture is 60%?

11[a]. What volume of liquid water forms when 10 lit of a mixture consisting of equal volumes of hydrogen and oxygen is exploded? Which gas remains after the explosion?

8.4. Water

Water is hydrogen oxide in which hydrogen exhibits an oxidation state of +1 and oxygen of −2.

Physical Properties. Pure water is a colourless, odourless, and tasteless transparent liquid. It can exist in one of three states of aggregation: a solid—ice, liquid water, and a gas—water vapour or steam. At 0 °C, the solid and liquid phases are in a state of dynamic equilibrium, therefore the melting point of ice is 0 °C. At 100 °C, the liquid and gaseous phases are in equilibrium (at STP). The boiling point of water is 100 °C. At +4 °C, it has the greatest density equal to 1 g/cm^3. Above or below this temperature, the density of water is less than 1 g/cm^3. This feature distinguishes

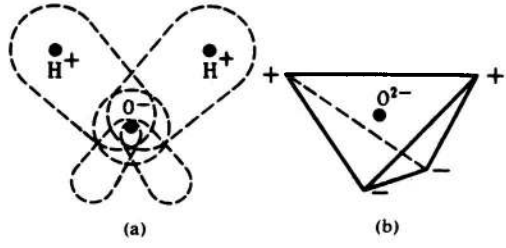


Fig. 27
Structure of water molecules:
a—arrangement of electron orbits; *b*—overall shape

water from all other substances, whose density diminishes with lowering of the temperature. When water solidifies, its volume grows and its density lowers: 92 volumes of liquid water yield 100 volumes of ice. The water molecule is polar and has a triangular structure. The electronegative oxygen atom is at the apex of the triangle, and the hydrogen atoms are at the corners of the base (Fig. 27). The bond angle is 104.5°.

Water molecules interact with one another and form a hydrogen bond. This is called the **association of water**. In the vapour state, the relative molecular mass (molecular weight) of water is 18, which corresponds to the formula H_2O. In liquid water at 4 °C, the molecular mass is 36, and at 0 °C it is 54. Hence, at 4 °C two water molecules are associated—$(H_2O)_2$, and at 0 °C—three—$(H_2O)_3$.

Chemical Properties. The polarity and small size of the water molecule determine its strong hydrating properties. **Hydration** is defined as the attachment of water to a substance.

Water molecules can attach themselves to various ions and form hydrates. Examples are the crystal hydrates $CuSO_4 \cdot 5H_2O$, $Na_2SO_4 \cdot 10H_2O$, and $FeSO_4 \cdot 7H_2O$.

Hydration occurs when water reacts with oxides, which results in the formation of a base or acid:

$$CaO + H_2O = Ca(OH)_2$$
$$P_2O_5 + 3H_2O = 2H_3PO_4$$

Unlike hydration, hydrolysis, which also occurs with the participation of water, leads to the decomposition of a substance. Water has a strong ionizing effect on the electrolytes dissolved in it and causes their dissociation.

Water both in the cold and with heating reacts actively with many metals preceding hydrogen in the electromotive series. In these reactions, the rele-

vant oxides or hydroxides form, and hydrogen is displaced:

$$2Fe + 3HOH = Fe_2O_3 + 3H_2\uparrow$$
$$2Na + 2HOH = 2NaOH + H_2\uparrow$$
$$Ca + 2HOH = Ca(OH)_2 + H_2\uparrow$$

Questions and Problems

1. Write equations of reactions characterizing each property of water. Consider these reactions from the viewpoint of oxidation and reduction processes.
2. Note the role of water in the process of electrolytic dissociation.
3. What is the role of water in hydrolysis?
4[a]. How many times does the volume of water increase when it passes from the liquid state into the gaseous one?
5[a]. Calculate the per cent concentration by mass of phosphoric acid in a solution obtained by dissolving 71 g of P_2O_5 in 129 g of water.
6[a]. In 600 g of a 10% solution of H_3PO_4 there were dissolved 142 g of P_2O_5. What was the per cent concentration by mass of the phosphoric acid in the obtained solution?

SUMMARY

Hydrogen occupies the first position in the periodic table of the elements. The features of structure of the hydrogen atom enable one to formally consider it as an analogue of the halogens. The typical hydrogen reactions are those in which it gives up an electron and forms the H^+ ion, or gains an electron and forms the hydride ion H^-. The most widespread compound of hydrogen is water. Its molecule is constructed according to the polar covalent type of bond and has a triangular shape with a bond angle of 104.5°. Water molecules form associations owing to hydrogen bonds. Hydration and hydrolysis are of the greatest practical significance among the chemical properties of water. Active metals reduce hydrogen from water, while the halogens oxidize its oxygen.

CHAPTER 9

THE HALOGENS

OBJECTIVES

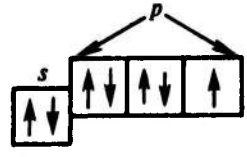
To establish the specific manifestations of analogy in the properties of the halogens and their compounds; to substantiate these laws from the standpoints of the previously studied theories; to make an argumented conclusion on the features characterizing the natural group of halogens on the basis of the cited facts.

9.1. General

The halogens are a natural group of analogous elements in Subgroup VIIA of the periodic table.

The halogens include fluorine F, chlorine Cl, bromine Br, iodine I, and astatine At. The first four elements occur in nature in the form of various compounds. Astatine has been obtained only artificially and is radioactive (its half-life is 8.3 h).

Each of the halogens has seven electrons with the configuration s^2p^5 in its outer energy level:

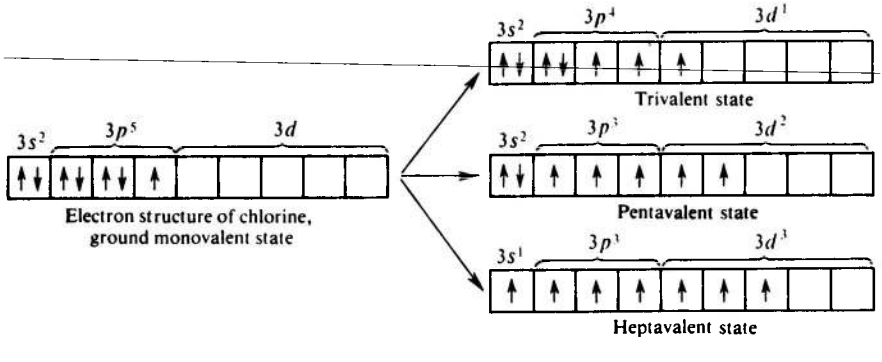


The shell of fluorine preceding the outermost one contains two electrons, of chlorine—eight, and of bromine, iodine, and astatine—18 electrons each. The halogens belong to *p* family elements.

The electron configurations of the halogen atoms are given below:

$_{9}F—1s^22s^22p^5$	(2nd period)
$_{17}Cl—1s^22s^22p^63s^23p^5$	(3rd period)
$_{35}Br—1s^22s^22p^63s^23p^63d^{10}4s^24p^5$	(4th period)
$_{53}I—1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^5$	(5th period)

The presence of one unpaired electron in the outer shell indicates that the halogens have a valence of 1 in the ground, unexcited, state. The outer shell of fluorine consists only of 2*s* and 2*p* sublevels, whereas the atoms of the remaining halogens have vacant boxes of the *d* sublevel in their outer shells. Consequently, with the exception of fluorine, the number of unpaired electrons in an atom of a halogen may grow to seven when the atom becomes excited, which is shown below:



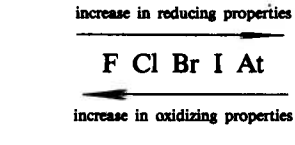
Within each period, the halogens are the most electronegative elements having the greatest electron affinity.

Within the halogen subgroup, the atomic radius grows when going down from fluorine to iodine.

The elements of this subgroup relate to the non-metals; with an increase in the charge of the nucleus from F to At, the non-metallic properties weaken, which is shown by the reduction in the ionization energy and the electron affinity.

The most typical of the halogens are compounds in which they exhibit their most stable oxidation state, -1. This is why the hydrogen compounds of the halogens are more stable than their oxygen ones. On the other hand, the halogens, except fluorine, can exhibit oxidation states from $+1$ to $+7$.

It is easy to understand the oxidation-reduction properties and differences in the chemical behaviour of the halogens by comparing these properties depending on the change in the charge of the nucleus when passing from fluorine to iodine. In the series F, Cl, Br, I, iodine has the largest atomic radius (and, therefore, the smallest electron affinity). Consequently, its oxidizing properties are less pronounced than those of bromine, chlorine, and fluorine. This is why the oxidizing properties of neutral atoms in the halogen subgroup diminish from fluorine to iodine, while the reducing properties grow:



Such a consecutive change in the properties is called monotonic.

The most widespread halogen in nature is chlorine. The most abundant compounds and minerals containing chlorine are rock salt NaCl, sylvinite $NaCl \cdot KCl$, bischofite $MgCl_2 \cdot 6H_2O$, carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$, etc. The water of the seas and oceans contains from 0.8 to 3.5% of NaCl.

The next in its abundance is fluorine, which is encountered most frequently as fluorspar (fluorite) CaF_2, and in the minerals cryolite Na_3AlF_6 and fluorapatite $Ca_3(PO_4)_2 \cdot CaF_2$. Bromides always accompany chlorine compounds, and are also contained in sea water. Iodine occurs together with chlorides and bromides, but its content is much lower. The richest sources of iodine are seaweeds and the water of petroleum fields.

Questions and Problems

1. How can one explain the term "non-metallic properties of elements"?
2. How do the properties of the halogens depend on their atomic radii?
3. Why does fluorine have the highest oxidation activity among the halogens?

4. What are the common and distinguishing features of the ions F^-, Cl^-, Br^-, and I^-?
5. Explain the laws of the changes in the physical properties of the halogens.
6. Use specific examples to prove the monotonic nature of the change in the properties of the halogens and explain what this depends on.

9.2. Preparation

The most important way of preparing fluorine is the electrolysis of fluorides, when fluorine evolves on the anode:

$$2F^- - 2e^- \rightarrow F_2$$

At present, potassium hydrogen fluoride KHF_2 is the main source of fluorine production.

Chlorine is customarily prepared in the laboratory by heating a mixture of hydrochloric acid with various oxidizing agents. Generally MnO_2, $KMnO_4$, and $KClO_3$ are used for this purpose:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$
$$2KMnO_4 + 16HCl = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O$$
$$KClO_3 + 6HCl = 3Cl_2 + KCl + 3H_2O$$

Chlorine is produced commercially by the electrolysis of sodium chloride. Gaseous chlorine evolves on the anode:

$$2NaCl + 2H_2O \xrightarrow{\text{el. current}} 2NaOH + H_2\uparrow + Cl_2\uparrow$$

Hydrogen and sodium hydroxide form in addition to chlorine.

The most favoured reaction for preparing bromine is that of its replacement in bromides:

$$2KBr + Cl_2 = 2KCl + Br_2$$

The main commercial sources of iodine are seaweeds and petroleum field water:

$$2NaI + MnO_2 + 3H_2SO_4 = I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O$$

The production of iodine from natural sources consists in transferring it into the molecular state:

$$2NaI + 2NaNO_2 + 2H_2SO_4 = I_2 + 2H_2O + 2NO + 2Na_2SO_4$$

Under laboratory conditions, bromine and iodine are prepared in the same way, namely, by reacting manganese(IV) oxide with bromides or iodides in an acid solution, for instance:

$$MnO_2 + 2KBr + 2H_2SO_4 = MnSO_4 + Br_2 + K_2SO_4 + 2H_2O$$

Questions and Problems

1. Consider the cited ways of preparing free halogens from the viewpoint of oxidation-reduction reactions. Compile an electron balance for each equation, and also use the ion-electron method. Indicate the oxidizing and reducing agents.

2. Explain the electrolysis of a melt and solution of KHF_2 and NaCl.

3. Chlorine can be obtained by the unbalanced equation

$$K_2Cr_2O_7 + HCl \rightarrow CrCl_3 + KCl + Cl_2 + H_2O$$

Balance the equation using the electron balance method and the ion-electron method.

4. Balance the following equation and indicate the oxidizing and reducing agents:

$$KI + KIO_3 + HCl \rightarrow KCl + I_2 + H_2O$$

5*. How many grammes of HCl reacted with MnO_2 if the evolved chlorine displaced 37.1 g of iodine from a KI solution?

6. Explain why fluorine cannot be used to displace heavier halogens from their salts.

7*. What masses of MnO_2 and a 30% solution of HCl are needed to produce 9 lit of chlorine?

9.3. Properties

The molecules of the simple substances formed by the halogens consist of two atoms joined by a covalent bond.

Physical Properties. An increase in the charge of the nucleus (atomic number) from fluorine to iodine is attended by elevation of the melting and boiling points and a growth in the electrical conductance (Table 4). The halogens have a pungent odour and are poisonous.

The halogens dissolve differently in water and in organic solvents. Fluorine dissolves in liquid hydrogen. Chlorine and bromine dissolve in water

Table 4

Physical Properties of the Halogens

Halogen	State of aggregation	Colour	Boiling point, °C	Melting point, °C	H_{diss} of Hal_2, kJ/mol	Internuclear distance, nm
F_2	Gas	Light yellow	−187	−223	159	0.142
Cl_2	Gas	Greenish yellow	−34.6	−101.6	243	0.200
Br_2	Liquid	Reddish brown	58.7	−7.3	193	0.229
I_2	Solid	Grayish black	184	113.5	151	0.267
At	Solid	—	299	411	117	—

(chlorine water, bromine water), in ethanol, and in ether. Iodine dissolves sparingly in water, and readily in ether, chloroform, and ethanol.

Chemical Properties. Fluorine can only be an oxidizing agent, which is easily explained by its position in the periodic table.

The halogens react with almost all simple substances. Their reactions with metals proceed the most vigorously.

When heated, fluorine reacts with all the metals (including gold and platinum); in the cold it reacts with the alkali metals, lead, and iron. It does not react with copper and nickel in the cold because a protective film of the fluoride forms on the metal surface and protects it from further oxidation.

Chlorine reacts vigorously with the alkali metals, while when heated it reacts with copper, iron, and tin. Bromine and iodine behave similarly.

The reaction of the halogens (Hal) with metals (M) is exothermic and can be expressed by the equation:

$$2M + nHal_2 \rightarrow 2MHal_n;\ \Delta H < 0$$

The metal halides are typical salts.

Under ordinary conditions, fluorine reacts with hydrogen in the dark with an explosion. Chlorine reacts with hydrogen in bright sunlight, and also when heated (for the mechanism of the reaction, see Sec. 8.3).

Bromine reacts with hydrogen only when heated, while iodine reacts with hydrogen with strong heating (up to 350 °C), but the process is reversible.

Fluorine also reacts with other non-metals to form fluorides:

$$Si + 2F_2 = SiF_4$$

Fluorine does not react directly with oxygen and nitrogen.

Chlorine also reacts actively with non-metals except for oxygen, nitrogen, and the noble gases:

$$2P + 3Cl_2 = 2PCl_3,\ \Delta H < 0$$

These reactions, like those for fluorine, are exothermic.

The chemical activity of bromine and iodine relative to non-metals is less pronounced than in fluorine and chlorine.

In all the above reactions, the halogens exhibit oxidizing properties. Fluorine is the most vigorous oxidizing agent. Even such stable substances as water and SiO_2 become oxidized in a fluorine atmosphere:

$$2H_2O + 2F_2 = 4HF + O_2$$

$$SiO_2 + 2F_2 = SiF_4 + O_2$$

Both reactions are exothermic. It is typical that oxygen evolves when these substances are oxidized.

Questions and Problems

1. What are the valence and oxidation state of the elements in molecules of the free halogens?
2. Which of the molecules F_2, Cl_2, Br_2, and I_2 is the most stable?
3. Consider the reaction equations treated in the present section from the viewpoint of oxidation-reduction.
4. Compile equations of the reactions of chlorine with magnesium, aluminium, iron, sulphur, and hydrogen and explain them from the viewpoint of oxidation-reduction.
5. Write the reversible reaction of iodine with hydrogen and indicate the conditions of shifting equilibrium in the direction of the product.
6. What facts can be used to prove that the oxidizing activity of the halogens decreases from fluorine to iodine? Write the reaction equations.

9.4. Hydrogen Compounds

The compounds of the halogens with hydrogen HHal, where Hal is any halogen, are called **hydrogen halides**. Owing to the high electronegativity of the halogens, the bonding electron pair is displaced in their direction, hence the molecules of these compounds are polar.

The hydrogen halides are colourless gases with a pungent odour that readily dissolve in water. At 0 °C, 500 volumes of HCl, 600 volumes of HBr, or 450 volumes of HI dissolve in one volume of water. Hydrogen fluoride mixes with water in any proportions.

The high solubility of these compounds in water enables concentrated solutions to be obtained. When dissolved in water, the hydrogen halides dissociate like acids. Hydrogen fluoride relates to the weakly dissociating compounds, which is explained by the especially strong bond in the molecule. The hydrogen halides are strong acids. Their salts are called fluorides, chlorides, bromides, and iodides, respectively. Dry hydrogen halides do not act on most metals.

Hydrofluoric acid decomposes glass and silicates:

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

and therefore it must never be stored in glass vessels. Apart from platinum and gold, hydrofluoric acid acts on all metals and oxidizes them. These reactions generally proceed only on the surface of a metal. The formed fluoride prevents the further proceeding of the reaction.

Hydrochloric acid, like other strong acids, reacts vigorously with many metals, their oxides and hydroxides. It does not react with metals located after hydrogen in the electromotive series.

In their chemical properties, HBr and HI are similar to HCl.

The hydrohalic acids differ substantially in their relation to oxidizing agents. The halide ions Hal^- except for fluoride are reducing agents:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

$$2KMnO_4 + 10KI + 8H_2SO_4 = 2MnSO_4 + 5I_2 + 6K_2SO_4 + 8H_2O$$

$$6KBr + K_2Cr_2O_7 + 7H_2SO_4 = 3Br_2 + 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

The reducing ability of the hydrohalic acids and their salts grows in the sequence Cl^-, Br^-, and I^-.

Preparation. Hydrogen fluoride HF is prepared by reacting concentrated sulphuric acid with fluorspar:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

A solution of hydrogen fluoride containing 40% of HF is called hydrofluoric acid.

Hydrogen chloride HCl is prepared by the direct reaction of hydrogen with chlorine:

$$H_2 + Cl_2 = 2HCl$$

or by the sulphate method based on the reaction of concentrated sulphuric acid with NaCl. In the cold, the reaction proceeds with the formation of HCl and $NaHSO_4$:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl\uparrow$$

The second step of the reaction proceeds when the reaction mixture is heated:

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl\uparrow$$

The sulphate method of preparing HCl involves a substantial outlay associated first of all with the appreciable consumption of sulphuric acid. This is why the main method of producing HCl at present is by direct synthesis from hydrogen and chlorine.

In the air, HCl forms droplets of a mist (fumes) when it comes in contact with the water vapour always present in the atmosphere. An aqueous solution of HCl is called hydrochloric acid.

Hydrogen bromide and hydrogen iodide are prepared by the hydrolysis of PBr_3 and PI_3:

$$PBr_3 + 3HOH = 3HBr + H_3PO_3$$

$$PI_3 + 3HOH = 3HI + H_3PO_3$$

Questions and Problems

1. What is the relation between the change in the atomic radius from fluorine to iodine and the properties of the hydrogen halides?

2. Describe the properties of hydrochloric acid and support your answer with reaction equations. Consider each of them from the viewpoints of ionic reactions and the oxidation-reduction theory.

3. Disclose for each of the oxidation-reduction reactions given in the present section the procedure of balancing them by the electron balance and ion-electron methods. Prove that the halogen ions in these reactions exhibit reducing properties.

4. Why is it impossible to prepare HBr and HI like HCl by displacement from their dry salts by concentrated sulphuric acid?

5*. The hydrogen chloride evolved when reacting sulphuric acid with 14.9 g of KCl was passed into a solution containing 8 g of sodium hydroxide, and then the solution was evaporated until dry. What are the mass and composition of the residue?

6*. When sulphuric acid was reacted with 120.5 g of sodium chloride, 73 g of hydrogen chloride were obtained. What is the per cent concentration by mass of the impurities in the sodium chloride?

7*. When preparing hydrogen chloride, 57 g of it were obtained from sodium chloride containing 95.5% of NaCl. What percentage by mass did this amount form of the theoretical yield?

8*. Calculate the per cent concentration by mass of HCl in a solution obtained by dissolving 4.48 lit of gaseous HCl in 12.7 ml of water.

9.5. Metal Halides

Most of the salts of hydrofluoric acid—fluorides—are sparingly soluble in water. Sodium, potassium, aluminium, tin, mercury, and silver fluorides dissolve well. *All the fluorides are poisonous*! Calcium fluoride CaF_2 is widely used to produce hydrofluoric acid, and also in metallurgy.

The salts of hydrochloric acid—chlorides—can be prepared in the following ways:

(1) by reacting a metal with chlorine:

$$Cu + Cl_2 = CuCl_2$$

(2) by reacting hydrochloric acid with a metal:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow$$

(3) by reacting a metal oxide or hydroxide with hydrochloric acid:

$$CuO + 2HCl = CuCl_2 + H_2O$$

$$KOH + HCl = KCl + H_2O$$

The chlorides of most metals dissolve well in water. Exceptions are Hg_2Cl_2, $CuCl_2$, AgCl, and $PbCl_2$.

The salts of hydrochloric acid have found numerous applications.

Sodium chloride NaCl, known in everyday life as table salt, is of major significance for the life of mankind. The Na^+ and Cl^- ions are the main ones in the fluids of a human organism. A 0.9% solution of NaCl, called a physiological solution, is widely used for levelling out and maintaining a normal osmotic pressure in an organism. Sodium chloride is the most important raw material for the production of chlorine, hydrochloric acid, sodium hydroxide, and other substances.

Potassium chloride KCl is employed for producing potassium hydroxide. The main consumer of KCl, however, is agriculture, where it is used as a fertilizer.

Calcium chloride $CaCl_2$ generally crystallizes in the form of the hexahydrate $CaCl_2 \cdot 6H_2O$. Calcium chloride is widely used in medicine as a haemostat in bleeding, to treat allergic diseases, and also as an antidote in poisoning by magnesium salts.

Silver chloride AgCl and bromide AgBr are used as light-sensitive substances in the fabrication of photographic films. This is based on their ability to decompose under the influence of light with the formation of free silver.

Zinc chloride $ZnCl_2$ is a poisonous compound. It is used as a preservative to protect wooden articles from decay, and also in the cellulose and paper industry.

The halide ions have a noticeable biological activity. For example, in animals and humans, fluorine is contained in the bone tissue and in the enamel of the teeth. A lack of fluorine in an organism causes a caries to develop (the gradual decay of bone tissue or a tooth).

Identification of the Hydrohalic Acids and Their Salts. Silver cations in the presence of dilute nitric acid precipitate the Cl^-, Br^-, and I^- anions from their solutions. The relevant reaction equations are:

$$Ag^+ + Cl^- = AgCl\downarrow$$
$$Ag^+ + Br^- = AgBr\downarrow$$
$$Ag^+ + I^- = AgI\downarrow$$

These reactions are thus qualitative ones.

AgF dissolves in water.

AgCl is a white curdy precipitate insoluble in water and nitric acid, but soluble in ammonia:

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$$

When the solution is acidified, the complex decomposes, and AgCl precipitates again:

$$[Ag(NH_3)_2]Cl + 2HCl = AgCl\downarrow + 2NH_4Cl$$

AgBr is a pale yellow precipitate insoluble in water and nitric acid and sparingly soluble in ammonia. It rapidly darkens.

AgI is a bright yellow precipitate.

Questions and Problems

1. Write the equations of the reactions for preparing magnesium chloride in all possible ways.

2. Give an example of an oxidation-reduction reaction where sodium iodide is the reducing agent.

3. Select reagents for a qualitative reaction to identify the chloride ion Cl^-. Propose different variants.

4*. To a solution containing 1.19 g of KBr there were added 2 g of silver nitrate. The precipitate was separated. What substances and in what amount were contained in the filtrate?

SUMMARY

The VIIA subgroup elements F, Cl, Br, I, and At are called the halogens. They have the same electron configuration of their outer level, i.e. ns^2np^5. This is why in compounds with metals and hydrogen they exhibit a stable oxidation state of -1.

Each halogen within its period has the highest electronegativity, electron affinity, and, consequently, non-metallic properties. But within the halogen subgroup itself, these properties change from fluorine to iodine monotonically, which is associated with the different charge of their nuclei.

Owing to the drop in the oxidizing activity from fluorine to iodine, each following halogen can be oxidized by the preceding one.

The products obtained when reacting the halogens with other elements are called halides. The metal halides—typical salts—should be considered as salts of the relevant hydrohalic acids HHal, where Hal is a halogen.

CHAPTER 10

THE OXYGEN SUBGROUP

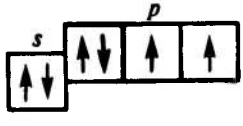
OBJECTIVES

To know the laws governing the properties of the oxygen subgroup elements; to be able to explain the similarities and differences of the elements in accordance with the structure of their atoms; to know the most important properties of oxygen and sulphur, as well as of their compounds.

10.1. General

Oxygen, sulphur, selenium, tellurium, and polonium form Subgroup VIA and are sometimes called the *chalcogens*.

The elements of this subgroup have six electrons in the outer energy level of an atom. Their configuration is s^2p^4, and they are distributed among the orbitals (boxes) as follows:



Below are given the electron configurations of the atoms:

$_8O$—$1s^2 2s^2 2p^4$ (2nd period)

$_{16}S$—$1s^2 2s^2 2p^6 3s^2 3p^4$ (3rd period)

$_{34}Se$—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$ (4th period)

$_{52}Te$—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^4$ (5th period)

$_{84}Po$—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^4$ (6th period)

The presence of two unpaired electrons in the outer level indicates a valence of two in the ground state. A comparison of the structure of the outer levels reveals that unlike oxygen, S, Se, Te, and Po have vacant orbitals in the *d* sublevel. The absence of free orbitals in the outer level of oxygen excludes the possibility of increasing the number of unpaired electrons, and therefore its only valence is two. The atoms of the other subgroup elements have vacant orbitals of the *d* sublevel in their outer level that can be occupied by excited *s* and *p* electrons of the same level. This explains why the number of unpaired electrons in sulphur and the remaining elements can be increased to four and six.

In their compounds with metals, the elements of the oxygen subgroup exhibit an oxidation state of -2.

In their oxygen compounds, sulphur, selenium, and tellurium exhibit oxidation states of $+4$ and $+6$, which correspond to two types of typical acid oxides, namely, RO_2 and RO_3, that form the acid H_2RO_3 and H_2RO_4.

We have already noted that when passing from oxygen to tellurium, the atomic radii grow, therefore this is attended by an increase in the reducing properties and weakening of the oxidizing ones. In the value of its electronegativity, oxygen gives way only to fluorine, therefore in reactions with all the other elements it exhibits only oxidizing properties. Sulphur, selenium, and tellurium in their properties relate to the group of oxidizing and reducing agents. In reactions with strong reducing agents, they exhibit oxidizing properties, while when reacted with strong oxidizing agents they become oxidized.

Oxygen, sulphur, selenium, and tellurium form hydrogen compounds of the general formula H_2R (H_2O, H_2S, H_2Se, and H_2Te).

Since the atomic radii increase from oxygen to tellurium, while the electron affinity decreases, in the series of compounds H_2R the polarity weakens from H_2O to H_2Te. All these compounds except water are gaseous. The strength of the bonds in H_2R diminishes from H_2O to H_2Te. The elements of this subgroup are in their lowest oxidation state in their hydrogen compounds, therefore they exhibit only reducing properties. They become oxidized consecutively, namely $E^{2-} \rightarrow E^0 \rightarrow E^{4+} \rightarrow E^{6+}$, and their reducing properties increase from H_2S to H_2Te.

The aqueous solutions of the compounds H_2R have weak acid properties. Dissociation occurs mainly in the first step:

$$H_2R \rightleftarrows H^+ + HR^-$$

Oxygen, sulphur, selenium, and tellurium are non-metals, but they are less active than the halogens. Polonium is a radioactive metal.

Questions and Problems

1. Compare the structure of the outer energy level of the atoms of the oxygen subgroup element with that of the halogens and indicate the different and similar features.
2. What oxidation states are possible for the oxygen subgroup elements? What are the features of oxygen?
3. In the compound OF_2, the oxygen is in the oxidation state of +2, while in its other compounds it is in the state of −2. Explain this behaviour of oxygen.
4. The reducing properties grow in the oxygen subgroup with an increase in the charge of the nucleus. Why?
5. Knowing the features of the structure of oxygen, sulphur, and selenium atoms, indicate which of the compounds H_2O, H_2S, and H_2Se is more polar and why.
6. Sulphur in the oxidation state of −2 exhibits only reducing properties, while in the oxidation states of +4 it exhibits both oxidizing and reducing properties. Why?

10.2. Oxygen

Oxygen is the most abundant element on the Earth. Molecular oxygen in the free state is contained in the air, where its content is 20.95% (by volume). Its content in the Earth's crust is 47.2% (by mass).

Oxygen is an important component of carbohydrates, fats, vegetable oils, and proteins. It occurs in the form of two allotropic modifications—molecular oxygen (dioxygen) O_2 and ozone (trioxygen) O_3. The molecule O_2, which has paramagnetic properties, is the most stable.

Under laboratory conditions, oxygen can be prepared in the following ways:

(a) by the decomposition of potassium chlorate:

$$2KClO_3 = 2KCl + 3O_2$$

(b) by the decomposition of potassium permanganate:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

(c) by heating the nitrates of the alkali metals ($NaNO_3$, KNO_3). Here only one-third of the oxygen contained in these compounds evolves in the free state:

$$2NaNO_3 = 2NaNO_2 + O_2$$

The main source for the commercial production of oxygen is air, which is liquefied and then separated into its fractions. First nitrogen boils out

(boiling point −195.8 °C), and almost pure oxygen remains in the liquid state because its boiling point is higher (−183 °C).

The method of producing oxygen based on the electrolysis of water is also in great favour.

Physical Properties. At STP, oxygen is a colourless, odourless, and tasteless gas. It boils at −183 °C, is heavier than air, and its density is 1.43 g/cm^3. One litre of water at STP dissolves 0.04 g of oxygen.

Chemical Properties. Occupying a position in the right upper corner of the periodic table, oxygen has sharply pronounced non-metallic properties. Having six electrons in its outer energy level, an oxygen atom can gain two electrons to fill its outer level to eight of them (the condition of the maximum chemical stability). This is why oxygen exhibits only oxidizing properties in reactions with other elements (except fluorine).

Oxygen forms compounds with all the chemical elements except helium, neon, and argon. It reacts with most elements directly, except for the halogens, gold, and platinum. The rate of the reaction of oxygen with both simple and compound substances depends on their nature, the temperature, and other conditions.

Such an active metal as cesium ignites spontaneously in the oxygen of the air already at room temperature.

Oxygen reacts actively with phosphorus when heated to 60 °C, with sulphur—to 250 °C, with hydrogen—to over 300 °C, and with carbon (in the form of coal or graphite) when heated to 700-800 °C:

$$4P + 5O_2 = 2P_2O_5; \qquad S + O_2 = SO_2$$
$$2H_2 + O_2 = 2H_2O; \qquad C + O_2 = CO_2$$

Hydrogen burns in oxygen according to a chain mechanism. The reaction begins with the formation of unstable active particles—free radicals—that are carriers of unpaired electrons:

$$H_2 + O_2 = \cdot OH + \cdot OH \text{ (chain initiation)}$$

The radicals ·OH readily react with an H_2 molecule:

$$\cdot OH + H_2 = H_2O + H\cdot$$

The hydrogen atom further reacts with an O_2 molecule to again form an ·OH radical and an oxygen atom, and so on. These elementary events facilitate the propagation of the chain.

When compound substances burn in an excess of oxygen, the oxides of the relevant elements form. For example, hydrogen sulphide H_2S, methane CH_4, ethanol C_2H_5OH, and pyrite FeS_2 burn as follows:

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O; \quad CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O; \quad 4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

These reactions are attended by the evolution of both heat and light, and it is just such reactions that are called burning or combustion.

In addition to the above type of reaction, there are also reactions attended only by the evolution of heat, without any light. They include the process of breathing first of all.

The Role of Oxygen in Nature and Its Application in Engineering. Oxygen participates in one of the most important vital processes—respiration. The oxidation of carbohydrates, fats, and proteins by oxygen is a source of energy for living organisms. The oxygen content in a human organism is 61% of the total mass of the body. It is contained in the form of various compounds in all the organs, tissues, and biological fluids.

A human inhales 20-30 m^3 of air a day.

Oxygen is widely used in practically all the branches of the chemical industry, for example in the production of nitric and sulphuric acids, organic synthesis, and in ore roasting processes.

The production of steel is impossible without oxygen; metallurgy consumes over 60% of all the oxygen used in industry.

The burning of hydrogen in oxygen is attended by the evolution of a considerable amount of energy, almost 286 kJ/mol. This reaction is used for welding and cutting metals.

Liquid oxygen is employed in the production of explosive mixtures.

The enormous demand for oxygen confronts mankind with a serious ecological problem, namely, the retaining of its stocks in the atmosphere. To date, the only source replenishing the atmosphere with oxygen is the vital activity of green plants. This is why it is especially important to preserve their amount on the Earth.

Questions and Problems

1. Explain why oxygen does not react directly with the halogens.
2. Give examples of the chain reactions you have studied.
3. Compile the thermodynamic equation of the burning of hydrogen in oxygen.
4. Write the equation of the reaction of water electrolysis yielding oxygen.
5. Compile the electron balance to the reaction equations given in the present section.

10.3. Sulphur

Sulphur is one of the few chemical elements used by mankind for already several thousand years. It occurs abundantly in nature and is found in both the free state (elemental sulphur) and in compounds. The sulphur-containing minerals can be divided into two groups—sulphides (pyrites, glances, and blendes), and sulphates.

The minerals of the first group include lead glance PbS, copper glance

Cu_2S, silver glance Ag_2S, zinc blende ZnS, cadmium blende CdS, pyrite FeS_2, and chalcopyrite $CuFeS_2$.

The minerals of the second group include gypsum $CaSO_4 \cdot 2H_2O$ and kieserite $MgSO_4 \cdot H_2O$.

When producing sulphur from its native compounds, for instance from pyrite, the latter is heated to high temperatures. The pyrite decomposes with the formation of iron(II) sulphide and sulphur:

$$FeS_2 = FeS + S$$

Sulphur can be obtained by oxidizing hydrogen sulphide with insufficient oxygen by the reaction

$$2H_2S + O_2 = 2S + 2H_2O$$

A widespread way of producing sulphur at present is by using carbon to reduce sulphur dioxide SO_2—a by-product in the melting of metals from sulphur-bearing ores:

$$SO_2 + C = CO_2 + S$$

The flue gases of metallurgical and coke furnaces contain a mixture of sulphur dioxide and hydrogen sulphide. The mixture is passed over a catalyst at a high temperature:

$$2H_2S + SO_2 = 2H_2O + 3S$$

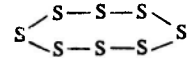
This oxidation-reduction reaction yields sulphur and water.

Physical Properties. Sulphur is a lemon-yellow solid. It is insoluble in water, but dissolves readily in carbon disulphide CS_2.

It has several allotropic modifications, namely, rhombic, monoclinic, and plastic sulphur. Rhombic sulphur, the most stable modification, consists of octahedral crystals. Monoclinic sulphur in the form of dark yellow acicular crystals is obtained when molten sulphur is cooled slowly. Plastic sulphur is an amorphous modification.

The experimental determination of the molecular mass of rhombic and monoclinic sulphur has revealed that sulphur molecules consist of eight atoms notwithstanding the difference in the modifications. Hence, the difference in the properties of these allotropic modifications is due not to a different number of atoms in a molecule (as in O_2 and O_3), but to the different structure of the crystals. Such a phenomenon is called **polymorphism.**

The atoms in a sulphur molecule form a closed ring with a bond angle of 108°:



Chemical Properties. Sulphur is comparatively inert in the cold, but elevation of the temperature increases its reactivity.

Sulphur exhibits oxidizing properties with metals. Sulphides form in these reactions:

$$Fe + S = FeS$$

Sulphur does not react with hydrogen at STP, but at 150-200 °C a reversible reaction proceeds:

$$H_2 + S \rightleftarrows H_2S$$

In its reactions with metals and hydrogen, sulphur behaves like a typical oxidizing agent, but in the presence of strong oxidizing agents it exhibits reducing properties:

$$S + 3F_2 = SF_6$$
$$S + O_2 = SO_2$$

Sulphur burns in oxygen at 280 °C, and in the air at 360 °C. The products are SO_2 and SO_3. Consequently, in its compounds with metals and hydrogen, sulphur exhibits an oxidation state of -2, and in its compounds with oxygen, $+4$ and $+6$.

Sulphur can also participate in disproportionation reactions. For example, when a sulphur powder is boiled with alkalies, sulphites and sulphides form:

$$3S + 6KOH = K_2\overset{+4}{S}O_3 + 2K_2\overset{-2}{S} + 3H_2O$$

Application. About half of the world's production of sulphur goes to manufacture sulphuric acid. The remainder is used in the rubber industry, in the production of artificial fibres, explosives, in industrial organic synthesis, and in agriculture.

Sulphur is a component of some very important amino acids. For instance, cysteine contains the SH group. Under definite conditions, cystine forms from two molecules of cysteine. In cystine, two cysteine molecules are joined by a disulphide bond (S—S). These bonds are needed to impart a definite configuration to the protein molecules. The transition S—S $\rightleftarrows$ SH occurs in the processes of hydrogen transfer in the cells. This reversible process protects an organism from radiation damage: the radicals H· and OH· appearing in cells when water is decomposed by the effect of radiation are trapped. Cystine forms in the hydrolysis of proteins forming tegumental tissues in humans and animals (from hair, wool, horns, etc.).

Questions and Problems

1. What stable oxidation states of sulphur do you know? Give examples of compounds and chemical reactions for producing sulphur.
2. Explain the balancing of the equations of oxidation-reduction reactions contained in this section by the electron balance and ion-electron methods. Do not forget that the latter is used only for reactions in solutions.
3. Write formulas of sulphur compounds with the sulphur exhibiting oxidation states of -2, $+4$, and $+6$.

10.4. Hydrogen Sulphide

Hydrogen sulphide is an analogue of water. Its electron dot formula  shows that two *p* electrons in the outer level of the sulphur atom participate in forming the bonds H—S—H. The H_2S molecule has an angular shape, therefore it is polar.

Hydrogen sulphide often accompanies petroleum and natural gas. It is also contained in the gases of volcanic eruptions and in the water of mineral springs.

Hydrogen sulphide is usually prepared by reacting dilute mineral acids with iron(II) sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S$$

Under ordinary conditions, hydrogen sulphide is a colourless gas with a strong characteristic smell of rotten eggs. It dissolves well in water: one volume of water dissolves 2.5 volumes of hydrogen sulphide.

An aqueous solution of H_2S is called hydrogen sulphide water.

Hydrogen sulphide solutions have an acid reaction owing to dissociation:

$$H_2S \rightleftarrows H^+ + HS^- \text{ or } H_2S + HOH \rightleftarrows H_3O^+ + HS^-$$
$$HS^- \rightleftarrows H^+ + S^{2-} \text{ or } HS^- + HOH \rightleftarrows H_3O^+ + S^{2-}$$

Generally the first step predominates. Hydrogen sulphide is a very weak acid; it is weaker than carbonic acid, which usually displaces H_2S from sulphides.

When heated, H_2S decomposes with the formation of sulphur and hydrogen:

$$H_2S = H_2 + S$$

The oxidation state of sulphur in H_2S is -2, therefore hydrogen sulphide generally exhibits reducing properties. Being a vigorous reducing agent, it is usually oxidized to $\overset{0}{S}$, $\overset{+4}{S}$, and $\overset{+6}{S}$.

For example, when reacting with oxygen, hydrogen sulphide may be oxidized either to free sulphur or to SO_2. In a mixture with insufficient oxygen, sulphur and water form:

$$2H_2S + O_2 = 2S + 2H_2O$$

This reaction is customarily used to produce sulphur from various gases containing hydrogen sulphide. In an excess of oxygen, hydrogen sulphide burns with the formation of water and sulphur dioxide:

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

Reactions with the halogens yield the relevant hydrohalic acids:

$$Br_2 + H_2S = S + 2HBr$$

Various oxidizing agents react vigorously with hydrogen sulphide. Free sulphur forms when it reacts with nitric acid:

$$H_2S + 2HNO_3 = S + 2NO_2 + 2H_2O$$

Hydrogen sulphide is very poisonous. When it is inhaled, it combines with haemoglobin and causes paralysis, which quite often is fatal. It is less dangerous in small concentrations.

Hydrogen sulphide forms two types of salts, namely, normal ones—sulphides such as Na_2S and acid ones—hydrogen sulphides (hydrosulphides) such as NaHS. These salts can be obtained by reacting hydroxides with hydrogen sulphide, e.g.

$$2NaOH + H_2S = Na_2S + 2H_2O$$

and also by the direct reaction of sulphur with metals or by an exchange reaction of salts with H_2S. The alkali metal sulphides are colourless substances readily soluble in water. The heavy metal sulphides are insoluble in water.

Being salts of a weak acid, sulphides are greatly hydrolyzed in aqueous solutions. For example, the alkali metal sulphides when dissolved in water have an alkaline reaction:

$$Na_2S + HOH \rightleftarrows NaHS + NaOH$$

All the sulphides, like hydrogen sulphide itself, are vigorous reducing agents:

$$3PbS + 8HNO_3 = 3PbSO_4 + 4H_2O + 8NO$$

When heated, the sulphides react with oxygen and are oxidized to SO_2 or SO_4^{2-}; sometimes the metal is reduced:

$$2PbS + 3O_2 = 2PbO + 2SO_2$$

Questions and Problems

1. Hydrogen sulphide water becomes turbid when stored. Why? Is the decomposition of hydrogen sulphide an oxidation-reduction reaction? Defend your answer.

2. Compile the formula of the dissociation constant of hydrosulphuric acid for the first step and explain how the equilibrium of the dissociation can be shifted in the direction of ion formation.

3. Compile an equation of the reaction of lithium sulphide hydrolysis in the molecular and ionic forms.

4*. In 183 ml of water there were dissolved 11.2 lit of hydrogen sulphide. What is the per cent concentration by mass of the H_2S in the obtained solution?

5*. What volume of oxygen is needed for the complete oxidation of 5.1 g of hydrogen sulphide? How many grammes of SO_2 form?

10.5. Sulphur Dioxide. Sulphurous Acid

Sulphur dioxide SO_2 forms when sulphur is burned in the air or oxygen, and also when sulphides such as pyrite are roasted:

$$S + O_2 = SO_2$$

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

The oxidation of pyrite underlies the industrial production of SO_2.

In the laboratory, SO_2 is prepared from salts of sulphurous acid by reacting them with strong acids:

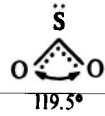
$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2\uparrow + H_2O$$

$$2NaHSO_3 + H_2SO_4 = Na_2SO_4 + 2SO_2\uparrow + 2H_2O$$

Sulphur dioxide also forms when concentrated sulphuric acid is reacted at an elevated temperature with metals having a low activity:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2\uparrow + 2H_2O$$

The SO_2 molecule has the structure of an isosceles triangle with the sulphur atom at the apex:



Under ordinary conditions, sulphur dioxide is a colourless gas with a characteristic pungent odour. It dissolves well in water. Aqueous solutions have an acid reaction because SO_2 reacts with water to form sulphurous acid H_2SO_3. The reaction is reversible:

$$SO_2 + H_2O \rightleftarrows H_2SO_3$$

A feature of SO_2 is its oxidation-reduction duality. The explanation is that in SO_2 sulphur is in the +4 oxidation state and therefore it can lose

two electrons and become oxidized to S(VI) or gain four electrons and become reduced to S. Which properties are exhibited depends on the nature of the reaction partner. For instance, with strong oxidizing agents, SO_2 behaves like a typical reducing agent. For example, halogens are reduced to the relevant hydrogen halides, while S(IV) generally transforms into S(VI):

$$\overset{+4}{S}O_2 + \overset{0}{Br}_2 + 2H_2O \rightarrow H_2\overset{+6}{S}O_4 + 2H\overset{-1}{Br}$$

In the presence of strong reducing agents, SO_2 behaves like an oxidizing agent:

$$SO_2 + 2H_2S = 3S + 2H_2O$$

It can also participate in a disproportionation reaction:

$$4SO_2 + 8KOH = 3K_2SO_4 + K_2S + 4H_2O$$

Sulphur dioxide is an acid oxide readily soluble in water (one volume of water dissolves 40 volumes of sulphur dioxide). An aqueous solution of SO_2 has an acid reaction and is called **sulphurous acid**. Usually, the main mass of the SO_2 dissolved in water is in the solution in the hydrated form $SO_2 \cdot H_2O$, and only an insignificant part of the dioxide reacts with water as follows:

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^- \rightleftarrows 2H^+ + SO_3^{2-}$$

Sulphurous acid is a dibasic (diatomic) one and forms two types of salts, namely, normal ones—sulphites, e.g. Na_2SO_3, and acid ones—hydrogen sulphites, e.g. $NaHSO_3$.

Sulphurous acid and its salts have both oxidizing and reducing properties, the property in each case being determined by the nature of the partner in a reaction. For example, in reactions with oxygen, sulphites are oxidized to sulphates:

$$2Na_2SO_3 + O_2 = 2Na_2SO_4$$

In the presence of more vigorous reducing agents, on the other hand, sulphites exhibit oxidizing properties:

$$Na_2\overset{+4}{S}O_3 + 3H_2\overset{-2}{S} = Na_2\overset{-2}{S} + 3\overset{0}{S} + 3H_2O$$

With strong heating, sulphites yield a disproportionation reaction:

$$4K_2SO_3 = 3K_2SO_4 + K_2S$$

Of the sulphites, only the salts of Group I *s* elements dissolve, and also hydrogen sulphites of the type $\overset{+2}{M}(HSO_3)_2$.

Since H_2SO_3 is a weak acid, the reaction of acids with sulphites and

hydrogen sulphites causes the evolution of SO_2. This method is customarily used to prepare SO_2 in a laboratory:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O$$

Sulphites dissolved in water readily hydrolyze. This increases the concentration of OH^- ions in the solution:

$$Na_2SO_3 + HOH \rightleftarrows NaHSO_3 + NaOH$$

Questions and Problems

1. Sulphur dioxide is a typical acid oxide. Characterize its properties and support your answer with reaction equations.
2. Write the formula of the dissociation constant of sulphurous acid for the first step. How can equilibrium be shifted in the direction of ion formation?
3. Compile the equation of the reaction of sodium sulphite hydrolysis. Write the formula of the equilibrium constant of this reaction (first step). How can hydrolysis be increased or weakened?
4. Explain the balancing of the equations of the oxidation-reduction reactions contained in this section by the electron balance and ion-electron methods (by the latter if the reaction proceeds in a solution).
5[a]. How much sulphur dioxide can be obtained from 40 g of pyrite containing 40% of impurities?

10.6. Sulphur Trioxide. Sulphuric Acid, Sulphates

Sulphur trioxide is prepared by oxidizing sulphur dioxide by the oxygen of the air in the presence of catalysts. The reaction is reversible and proceeds with the evolution of heat, i.e. is exothermic:

$$2SO_2 + O_2 \rightleftarrows 2SO_3, \quad \Delta H < 0$$

In practice, the reaction is conducted at 400-500 °C in the presence of catalysts such as platinum, iron(III) oxide, vanadium(V) oxide, or silver vanadate $AgVO_3$.

The reaction of SO_2 with O_2 occurs on the surface of the catalyst (heterogeneous catalysis). This method of oxidizing SO_2 to SO_3 is called the **contact** one, and the reactors used for the process are **contact apparatus.**

Another way of oxidizing SO_2 to SO_3 is the use of nitrogen dioxide as the oxidizing agent:

$$SO_2 + NO_2 = SO_3 + NO$$

The formed nitrogen monoxide when it reacts with the oxygen of the air readily and rapidly transforms into the dioxide:

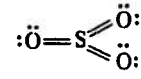
$$2NO + O_2 = 2NO_2$$

that can be used again for the oxidation of SO_2. Consequently, the NO_2 plays the role of an oxygen carrier. This process of oxidizing SO_2 to SO_3 is called the **lead chamber process.**

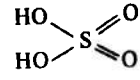
Sulphur trioxide is a colourless liquid solidifying at 16.8 °C. It dissolves very well in water and concentrated sulphuric acid. A solution of SO_3 in anhydrous sulphuric acid is called **oleum.** Oleum can contain from 30 to 70% of SO_3. It mixes with water in any proportions and forms a number of products, the most important of which is monohydrate or anhydrous sulphuric acid. The dissolution of sulphur trioxide in water is attended by the evolution of a considerable amount of heat:

$$SO_3 + H_2O = H_2SO_4; \quad \Delta H = -89.1 \text{ kJ/mol}$$

The SO_3 molecule has a planar structure and can be represented as follows:



Sulphur trioxide is a typical acid oxide. When a water molecule is attached, one of the double bonds breaks to form two simple ones:



This is the structural formula of sulphuric acid. The latter is chiefly produced in the industry by the contact process. The raw material is pyrite FeS_2 from which sulphur dioxide is obtained by roasting:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

First the SO_2 is purified from any admixtures, and then in a mixture with air is fed into a contact apparatus where the SO_2 is oxidized to SO_3 when it comes in contact with a catalyst. The formed sulphur trioxide is then fed in counterflow into an absorbing tower where it is absorbed by concentrated sulphuric acid. As the latter becomes saturated, first anhydrous sulphuric acid forms, and then oleum. The oleum is subsequently diluted to 98% sulphuric acid and is delivered to customers.

Physical Properties of Sulphuric Acid. Anhydrous sulphuric acid is a colourless oily liquid crystallizing at +10.5 °C. It is almost twice as heavy (its density is 1.85 g/cm^3) as water, is odourless and not volatile.

Chemical Properties. Sulphuric acid mixes with water in any proportions and forms hydrates varying in composition from $H_2SO_4 \cdot H_2O$ to $H_2SO_4 \cdot 4H_2O$. The dissolution of sulphuric acid in water is attended by the evolution of a large amount of heat. To avoid splashing of the heated surface layer of the solution, *always pour sulphuric acid into water.* Concen-

trated sulphuric acid vigorously absorbs water, and is therefore used to dry gases. Its property of charring organic substances is also explained by the absorption of water.

Dilute sulphuric acid has all the typical properties of acids, but its reaction with simple substances has certain distinctions. This depends primarily on the concentration.

Concentrated sulphuric acid is a vigorous oxidizing agent. At elevated temperatures, it oxidizes most metals including copper, silver, and mercury. Depending on the activity of the metal, the reduction products may include sulphur in the oxidation states of -2, 0, and $+4$.

When heated with copper or other metals having a low activity, SO_2 forms:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

$$\begin{array}{l|l} \overset{0}{Cu} - 2e^- \rightarrow \overset{+2}{Cu} & 1 \\ \overset{+6}{S} + 2e^- \rightarrow \overset{+4}{S} & 1 \end{array}$$

$$\overset{0}{Cu} + \overset{+6}{S} \rightarrow \overset{+2}{Cu} + \overset{+4}{S}$$

With an active metal such as zinc, concentrated sulphuric acid reacts with the formation of various products:

$$Zn + 2H_2SO_4 = SO_2\uparrow + 2H_2O + ZnSO_4$$
$$3Zn + 4H_2SO_4 = S + 4H_2O + 3ZnSO_4$$
$$4Zn + 5H_2SO_4 = H_2S + 4H_2O + 4ZnSO_4$$

In the cold, concentrated sulphuric acid (above 93%) does not react with active metals such as aluminium, iron, and chromium. This is explained by passivation of the metals. This feature of sulphuric acid is widely used when transporting it in iron containers.

Concentrated sulphuric acid when boiling oxidizes sulphur and carbon:

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O$$
$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$

Dilute sulphuric acid dissociates in water:

$$H_2SO_4 = H^+ + HSO_4^-$$
$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$$

and is characterized by all the properties of acids. For example, it reacts only with metals preceding hydrogen in the electromotive series:

$$Zn + H_2SO_4(dil.) \rightarrow ZnSO_4 + H_2\uparrow$$

$$\overset{0}{Zn} - 2e^- \rightarrow Zn^{2+} \quad | \; 1$$

$$2H^+ + 2e^- \rightarrow \overset{0}{H_2} \quad | \; 1$$

$$\overset{0}{Zn} + 2H^+ \rightarrow Zn^{2+} + \overset{0}{H_2}$$

Such a reaction does not proceed with copper because the latter follows hydrogen in the electromotive series.

A comparison of the oxidizing properties of concentrated and dilute sulphuric acid reveals that the sulphate ion is the oxidizing agent in the concentrated acid, and the hydrogen ion in the dilute acid.

It is difficult to name a branch of chemical production that is not associated directly or indirectly with sulphuric acid. The latter most likely occupies first place among chemical compounds in the diversity of its applications. In the basic chemical industry, sulphuric acid is used in the production of fertilizers. It is widely used in metallurgy, machine-building, in the petroleum refining industry, in the production of organic substances such as polymers, dyes, and drugs.

Sulphuric acid forms two types of salts: normal ones—**sulphates**, e.g. Na_2SO_4, and acid ones—**hydrogen sulphates**, e.g. $NaHSO_4$.

Most of the salts dissolve well in water. The virtually insoluble sulphates include $BaSO_4$, $SrSO_4$, and $PbSO_4$. Barium sulphate also does not dissolve in dilute acids, therefore its formation is a qualitative identification reaction for the SO_4^{2-} ion: $BaSO_4$ precipitates in the form of white crystals. Most salts of H_2SO_4 are colourless, and crystallize well from solutions in the form of crystal hydrates. Sulphates behave differently when heated. Some of them such as Na_2SO_4, K_2SO_4, and $BaSO_4$ do not decompose even at 1000 °C, while others decompose into the relevant oxide and SO_3. The sulphates of metals(III), and also of the noble and seminoble metals decompose much more readily:

$$Al_2(SO_4)_3 = Al_2O_3 + 3SO_3$$

$$2HgSO_4 = 2Hg + 2SO_3 + O_2$$

The following sulphates are of major importance. **Sodium sulphate** Na_2SO_4 in the form of its crystal hydrate $Na_2SO_4 \cdot 10H_2O$ is known as Glauber's salt. It is widely used in the production of glass and in crystallography.

Glauber's salt is used in medicine as a purgative. It can also be used as an antidote in poisoning by barium and lead salts.

Calcium sulphate $CaSO_4$ is used in the form of the crystal hydrates: $CaSO_4 \cdot 2H_2O$—gypsum, and $2CaSO_4 \cdot H_2O$—alebaster. Gypsum can be transformed into alebaster by heating (150-170 °C). At a higher temperature the anhydrous salt forms. Alebaster is used as a binder in the building industry, in medicine to make bandages and splints for bone fractures, and in prosthetic dentistry to prepare models of artificial dentures.

Copper sulphate $CuSO_4$ vigorously combines with water to form the crystal hydrate $CuSO_4 \cdot 5H_2O$ called blue vitriol. It is employed in agriculture for controlling plant pests.

Zinc sulphate $ZnSO_4$ forms the crystal hydrate $ZnSO_4 \cdot 7H_2O$. It is used as a mordant in the dyeing of fabrics.

Iron(II) sulphate $FeSO_4$ forms the crystal hydrate $FeSO_4 \cdot 7H_2O$ and is called iron or green vitriol. It is used in agriculture to control pests.

As indicated above, the anion SO_4^{2-} can be identified qualitatively by the formation of a white finely crystalline precipitate of $BaSO_4$ that is insoluble in water and acids.

The salts of sulphuric acid are hydrolyzed only relative to the cation, or are not hydrolyzed at all.

Questions and Problems

1. Compile equations of reactions confirming that sulphur trioxide is an acid oxide.
2. Compile equations of reactions showing that sulphuric acid is a typical acid.
3. Write out the equations of the oxidation-reduction reactions and explain the balancing of the equations by the electron balance and ion-electron methods.
4. Explain the process of copper sulphate hydrolysis.
5. Compare the chemical properties of the acids H_2S, H_2SO_3, and H_2SO_4. Defend your answer using the relevant reaction equations.
6. How can the transformations FeS_2-SO_2-SO_3-H_2SO_4 be carried out? Write the equations of the relevant reactions.
7*. What mass of SO_3 is needed to dehydrate 50 g of a 95.5% solution of sulphuric acid?
8*. What mass of SO_3 must be dissolved in 200 g of a 95.5% solution of H_2SO_4 to obtain a 20% solution of oleum?
9*. In 40 g of 20% sulphuric acid, there were dissolved 60 g of SO_3. What is the per cent concentration by mass of the H_2SO_4 in the obtained solution?
10*. To a solution containing 10 g of NaOH there were added 30 g of a 30% sulphuric acid solution. What salt and what amount of it formed?
11*. What is the per cent concentration by mass of $FeSO_4$ in a solution prepared by dissolving 27.8 g of $FeSO_4 \cdot 7H_2O$ in 50 ml of water?
12*. A mixture of sodium chloride and sodium sulphate with a mass of 2.59 g was treated with concentrated sulphuric acid. There were obtained 2.84 g of sodium sulphate. What was the mass composition of the initial mixture?
13*. What mass of sulphuric acid can be produced from one tonne of pyrite containing 45% of FeS_2?

SUMMARY

The elements of Subgroup VIA include oxygen, sulphur, selenium, tellurium, and polonium, sometimes called the chalcogens. Their outer energy level has the configuration ns^2np^4. Oxygen in its compounds can exhibit only an oxidation state of -2 (except for OF_2), while the other elements of this subgroup can also be in the states of $+4$ and $+6$. This is explained by the presence of vacant *d* sublevels in the outer levels.

The atomic radii of these elements grow from oxygen to polonium, therefore the oxidizing properties weaken and the reducing ones increase. The elements of this subgroup form the hydrogen compounds H_2R.

Hydrogen sulphide H_2S is a typical reducing agent. In their oxygen compounds, the elements of this subgroup exhibit oxidation states of $+4$ and $+6$, which correspond to the oxides RO_2 and RO_3. Sulphur dioxide SO_2 exhibits both oxidizing and reducing properties. Sulphurous acid H_2SO_3 also exhibits such properties. Sulphur trioxide SO_3 is produced by the contact process in the production of sulphuric acid with the use of catalyst.

Sulphuric acid is dibasic and forms two types of salts—normal and hydrogen sulphates. Concentrated sulphuric acid when heated reacts with many metals following hydrogen in the electromotive series. Dilute sulphuric acid reacts with metals preceding hydrogen in this series.

CHAPTER 11

THE NITROGEN SUBGROUP

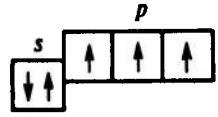
OBJECTIVES

To be able to explain the laws in the decrease of the non-metallic properties when passing from the halogens and oxygen subgroup to the elements of the nitrogen subgroup; to know the change in the properties of the elements within the subgroup and explain them in accordance with the structure of an atom; to have clear notions of the properties of the hydrogen and oxygen compounds of nitrogen, and also to know the properties of nitric acid.

11.1. General

Subgroup VA is formed by the *p* elements nitrogen N, phosphorus P, arsenic As, antimony Sb, and bismuth Bi.

The atoms of these elements have five electrons in their outer energy level with the configuration s^2p^3. These electrons are distributed as follows:

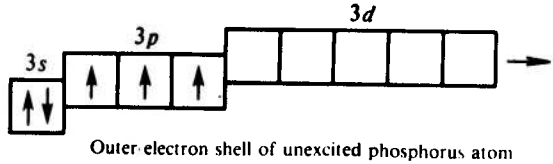


The shell of nitrogen below the outer one contains two electrons, that of phosphorus—eight, and those of arsenic, antimony, and bismuth—18 each.

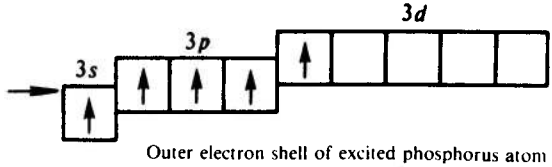
The electron configurations of these elements are as follows:

$_{7}N$—$1s^2 2s^2 2p^3$ (2nd period)
$_{15}P$—$1s^2 2s^2 2p^6 3s^2 3p^3$ (3rd period)
$_{33}As$—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ (4th period)
$_{51}Sb$—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$ (5th period)
$_{83}Bi$—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^3$ (6th period)

The presence of three unpaired electrons in the outer level indicates that the atoms of the main subgroup elements have a valence of three in the ground state. The outer level of nitrogen consists only of two sublevels—2*s* and 2*p*. The atoms of the remaining elements of this subgroup have vacant orbitals (boxes) of the *d* sublevel in their outer energy levels. Consequently, one of the *s* electrons of the outer level can pass into the *d* sublevel of the same level when excited, which leads to the formation of five unpaired electrons:



Outer electron shell of unexcited phosphorus atom



Outer electron shell of excited phosphorus atom

Hence, phosphorus, arsenic, antimony, and bismuth have five unpaired electrons in the excited state, and their valence in this state is five.

In a nitrogen atom, an electron cannot be excited in this way because the second level has no *d* sublevels. Consequently, nitrogen cannot be pentavalent, but it can form a fourth covalent bond by the donor-acceptor mechanism at the expense of the unshared electron pair $2s^2$.

A different process is also possible for a nitrogen atom. When one of the two 2*s* electrons is given up, the atom transforms into the singly charged tetravalent N^+ ion:



Neutral nitrogen atom — Singly charged and tetravalent

From nitrogen to bismuth, the radii of the atoms and the R^{3-} and R^{5+} ions grow, while the ionization energies diminish. The reducing properties of the neutral atoms increase from N to Bi, while the oxidizing properties decrease.

Nitrogen, phosphorus, and arsenic form polar compounds of the RH_3 type with hydrogen, exhibiting an oxidation state of -3.

But the ability to gain electrons is considerably less pronounced in them than in the relevant elements of Groups VI and VII. With oxygen, they form oxides of the R_2O_5 type exhibiting the highest positive oxidation state of $+5$.

Within the subgroup, the non-metallic properties diminish from nitrogen to bismuth, and the metallic properties grow. In antimony, these properties are equal, while in bismuth metallic properties predominate. Phosphorus, arsenic, and antimony form several allotropic modifications.

Questions and Problems

How can you explain that the valence of nitrogen cannot exceed four, while its oxygen state can be $+5$? At the same time, the valence of the other elements of the subgroup can be five, like the oxidation state.

11.2. Nitrogen

Nitrogen forms about four-fifths of the atmospheric air, i.e. 78.2% by volume. Of the nitrogen compounds, $NaNO_3$—sodium nitrate or Chile nitre forming large deposits along the Pacific Ocean coast of Chile—is of the greatest significance.

In the laboratory, nitrogen can be prepared from ammonium nitrite by thermal decomposition:

$$NH_4NO_2 = N_2\uparrow + 2H_2O$$

Nitrogen is produced on a commercial scale from liquefied air that is subjected to fractional distillation. First nitrogen separates (boiling point $-195.8\,°C$) because the boiling point of oxygen is considerably higher ($-183\,°C$).

Physical Properties. The nitrogen molecule is diatomic. Under ordinary conditions, N_2 is a colourless, odourless, and tasteless gas. At 0 °C, 100 ml

of water dissolve 2.33 ml of nitrogen. The nitrogen molecule is stable and does not decompose into atoms even at very high temperatures (at 3000 °C only 0.1%). Because of such stability, nitrogen has a low reactivity, giving way in this respect only to the noble gases. In other words, an inherent property of the molecules N_2 (N≡N) is their inertness.

A nitrogen atom can fill up its electron shell as follows:

(a) by gaining three electrons, which leads to the formation of nitride ions N^{3-};

(b) by forming simple two-electron bonds as in NH_3, or multiple bonds as in N≡N or NO_2;

(c) by the formation of two-electron bonds, which is typical of the NH_4^+ ion.

Chemical Properties. Under ordinary conditions, nitrogen reacts only with lithium and does not react with any of the other metals and non-metals:

$$6Li + N_2 = 2Li_3N$$

When heated, nitrogen reacts with other metals to form nitrides:

$$N_2 + 3Ca = Ca_3N_2$$

At high temperatures and in the presence of catalysts, the activity of nitrogen grows substantially, and it can exhibit both oxidizing $N_2 + 3H_2 \rightleftarrows 2NH_3$ and reducing properties. It reacts with oxygen at a temperature above 1500 °C:

$$N_2 + O_2 = 2NO$$

The difficulty of oxidizing nitrogen is explained by the very high energy of thermal dissociation of its molecule into atoms, while this, in turn, is due to the triple bond.

Application. Nitrogen is mainly used in the production of ammonia, nitric acid, and nitrogen fertilizers.

Questions and Problems

1. What factors can increase the reactivity of nitrogen? Explain the essence of their action on nitrogen.

2. Compare the chemical activity of nitrogen with that of oxygen and chlorine, and explain why the activity of nitrogen is considerably lower.

3[a]. Ammonium nitrite with a mass of 100 g was roasted for a while, after which its mass was equal to 93.6 g. How many litres of nitrogen evolved and what percentage of the salt by mass decomposed?

11.3. Ammonia

Ammonia is produced commercially by direct synthesis from nitrogen and hydrogen:

$$N_2 + 3H_2 = 2NH_3$$

The most optimal conditions for this reaction to proceed are the presence of a catalyst, a temperature of 500 °C, and a pressure of 2×10^4 kPa. The reaction is exothermic, therefore by Le Chatelier's principle equilibrium will shift more to the right when the temperature is lower. But at low temperatures, the catalyst loses its activity and the reaction rate is very low. Porous iron containing additions of oxides of aluminium, potassium, calcium, and silicon is used as the catalyst. The reaction is conducted at about 500 °C, with compensation of the resulting shift of equilibrium to the left by an increase in the pressure.

The industrial plants for ammonia synthesis operate with recycling of the unreacted nitrogen and hydrogen. After a reaction, the gas mixture is cooled, the ammonia contained in it condenses and is withdrawn, while the unreacted nitrogen and hydrogen are mixed with a fresh portion of the gases, the mixture is fed onto the catalyst, and so on. The withdrawal of ammonia from the reaction mixture shifts equilibrium to the right.

Ammonia is prepared in a laboratory by heating ammonium salts with alkalies:

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3\uparrow + 2H_2O$$
$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3\uparrow + 2H_2O$$

Physical Properties. Ammonia is a colourless poisonous gas with a typical suffocating smell. It dissolves very readily in water (one litre of water at 0 °C dissolves 1150 lit of NH_3). A solution of ammonia in water is called **ammonia water.**

Chemical Properties. Of the five electrons in the outer shell of nitrogen, only three *p* electrons participate in the formation of a chemical bond with hydrogen atoms (sp^3 hybridization).

The ammonia molecule NH_3 is polar and has the shape of a regular trihedral pyramid with the nitrogen atom at its apex. The unshared electron pair of the nitrogen atom creates conditions for the acceptance by the molecule of a proton according to the donor-acceptor mechanism, transforming it into the singly charged cation NH_4^+:

$$\ddot{N}H_3 + H^+ \rightarrow [NH_4]^+$$

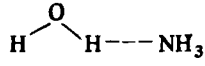
The positive charge is distributed uniformly in the formed cation. Ammonia follows this mechanism when reacting with water and with any other

substance capable of detaching protons, in particular with acids. In all these reactions, ammonia exhibits basic properties.

An aqueous solution of ammonia has an alkaline reaction because the attachment of an H^+ ion increases the concentration of OH^- ions:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

When the NH_4^+ and OH^- ions react, NH_3 and H_2O form again, i.e. the ionic compound NH_4OH (ammonium hydroxide) does not form. It would be more correct to consider that there is a hydrogen bond between the NH_3 and H_2O:



Gaseous ammonia also reacts with acids to form ammonium salts:

$$NH_3 + HCl = NH_4Cl$$

This reaction can proceed in the gas phase.

Since acids can lose a proton more readily than water, the concentration of the NH_4^+ ions in acidic solutions is considerably higher. An aqueous ammonia solution is a weak base.

Ammonium salts can be obtained by reacting not only gaseous ammonia with acids, but also aqueous ammonia solutions with acids.

Ammonia is a reducing agent. This can be explained by the nitrogen being in the -3 oxidation state; it can therefore readily be oxidized to N_2 or $\overset{+2}{N}$:

(a) halogens usually oxidize ammonia to free nitrogen:

$$8NH_3 + 3Br_2 = N_2\uparrow + 6NH_4Br$$

(b) in a mixture with oxygen, ammonia burns with a greenish-yellow flame:

$$4NH_3 + 3O_2 = 6H_2O + 2N_2\uparrow$$

(c) if the reaction with oxygen proceeds in the presence of a catalyst, the oxidation of NH_3 is attended by the formation of nitrogen monoxide:

$$4NH_3 + 5O_2 = 6H_2O + 4NO\uparrow$$

This reaction is of a major practical significance because it is used to produce nitric acid.

Ammonia vigorously reduces some metals from their oxides:

$$3CuO + 2NH_3 = N_2\uparrow + 3Cu + 3H_2O$$

Questions and Problems

1. Why does ammonia exhibit basic properties in a solution, while HCl and H_2S exhibit acidic ones?

2. Compare the attitude of ammonia, hydrogen sulphide, and hydrogen chloride to ammonia. Write the reaction equations. Explain the reasons for the similarity and difference.

3. Give examples confirming that the volatile hydrogen compounds of nitrogen, sulphur, and chlorine have reducing properties. Why are these properties not typical for water and hydrogen fluoride.

4. Compile the equations of the reactions of ammonia with sulphuric, nitric, and phosphoric acids (take into account the possibility of acid salts forming).

5. Are the reactions of ammonia with water and acids oxidation-reduction ones? Defend your answer.

6. Why should an ammonia solution never be stored next to hydrochloric acid?

7. Prove that ammonia has reducing properties.

8*. To prepare NH_4Cl, 35 g of ammonia and 73 g of hydrogen chloride were taken. What products formed and in what amount?

9*. In 24.9 ml of water, there were dissolved 6.72 lit of NH_3. What is the per cent concentration by mass of the NH_3 in the obtained solution?

10*. What volume of hydrogen is needed to produce 1.19 t of ammonia if the actual yield is 70% by mass of the theoretical one?

11*. Gaseous ammonia in a volume of 2.24 lit was absorbed by 20 g of a 49% phosphoric acid solution. What salt formed and in what amount?

11.4. Ammonium Salts

The NH_4^+ cation behaves like an ion of a monovalent metal. Ammonium salts are crystalline substances soluble in water, and in aqueous solutions they dissociate completely into ions:

$$(NH_4)_nX \rightleftarrows nNH_4^+ + X^{n-}$$

where X is an acid residue.

In the chemical respect, ammonium salts are reactive. For example, when heated with bases, they enter into an exchange reaction with the evolution of ammonia. This is a reaction for the qualitative identification of the ammonium ion:

$$NH_4Cl + NaOH = NaCl + NH_3\uparrow + H_2O$$

If a salt is formed by a volatile acid, it decomposes completely when heated, but when cooled the evolved gases again react to form the initial salt:

$$NH_4Cl(s) \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} NH_3(g) + HCl(g)$$

If a salt is formed by a non-volatile acid, partial decomposition occurs:

$$(NH_4)_2SO_4 = NH_3\uparrow + NH_4HSO_4$$

Ammonium salts in which the anion has pronounced oxidizing properties experience oxidation-reduction changes when heated, as a result of which the decomposition is irreversible:

$$NH_4NO_3 = N_2O\uparrow + 2H_2O$$

Ammonium salts have found many applications.

Ammonium chloride NH_4Cl (sal ammoniac) is used in soldering and tin-plating metals, and in the fabrication of galvanic cells.

Ammonium sulphate $(NH_4)_2SO_4$ and **ammonium nitrate NH_4NO_3** are used as fertilizers, the content of assimilatable nitrogen in the nitrate being higher than in other ammonium salts. Ammonium nitrate combined with combustible substances (for example, with coal and aluminium) is employed as an explosive (ammonals).

Ammonium hydrogen carbonate NH_4HCO_3 is employed at bakeries (mainly when baking cakes and the like) to impart the required porosity to the dough. Its action is based on its ability to decompose with the evolution of gases, which is what produces the porosity:

$$NH_4HCO_3 = NH_3\uparrow + CO_2\uparrow + H_2O$$

Questions and Problems

1. What are the oxidation state and valence of the nitrogen atom in ammonium chloride?
2. Compile the equations of the decomposition reactions of the following salts: ammonium chloride, ammonium carbonate, ammonium nitrite, and ammonium nitrate. In what respects are these reactions similar and in what are they different?
3. Write out from the text of this section the oxidation-reduction reactions. Explain their balancing by the electron balance and ion-electron methods.
4. A solution of ammonia in water has the properties of a weak base. Explain how the hydrolysis of ammonium sulphate and ammonium carbonate proceeds. What will the pH be in the solutions of these salts?
5*. When ammonia was passed into 20 g of a sulphuric acid solution, 6.6 g of ammonium sulphate were obtained. What was the per cent concentration by mass of the acid in the initial solution?
6*. To prepare ammonium chloride, 35 g of ammonia and 73 g of hydrogen chloride were taken. Calculate the mass of the formed NH_4Cl. Which substance and how many grammes remained after the reaction?
7*. A mixture of NH_4Cl and NaCl with a mass of 11.2 g was roasted to a constant mass of 5.85 g. How many grammes of sodium chloride were contained in the mixture and what was the mole ratio of the components?

11.5. Nitrogen Oxides

Nitrogen forms the following oxides: dinitrogen monoxide N_2O, nitrogen monoxide NO, dinitrogen trioxide N_2O_3, nitrogen dioxide NO_2, and dinitrogen pentoxide N_2O_5, in which it is in the oxidation states from +1 to +5.

Dinitrogen monoxide N_2O is obtained when ammonium nitrate decomposes:

$$NH_4NO_3 = N_2O + 2H_2O$$

Dinitrogen monoxide is a colourless gas with a weak sweetish odour, well soluble in water. At 700 °C, it decomposes into nitrogen and oxygen:

$$2N_2O = 2N_2 + O_2$$

This is why N_2O is an oxidizing agent with respect to all substances that react directly with oxygen:

$$N_2O + H_2 = N_2 + H_2O$$

Nitrogen monoxide NO is obtained in the industry in the catalytic oxidation of ammonia:

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

In a laboratory, NO can be prepared by reacting 30-35% nitric acid with copper:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Nitrogen monoxide is a colourless gas that is difficult to compress. It dissolves poorly in water and relates to the indifferent oxides. Nitrogen monoxide has both oxidizing and reducing properties. The oxygen readily oxidizes it to NO_2:

$$2NO + O_2 = 2NO_2$$

In the presence of reducing agents, it behaves like an oxidizing agent:

$$2NO + 2SO_2 \rightleftarrows 2SO_3 + N_2$$

Nitrogen monoxide is used in the production of nitric acid.

Dinitrogen trioxide N_2O_3 forms when NO_2 reacts with NO (the reaction is reversible):

$$NO_2 + NO \rightleftarrows N_2O_3$$

Dinitrogen trioxide is an acid oxide, hence it readily reacts with alkalies to form nitrites—salts of nitrous acid:

$$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O$$

Nitrogen dioxide NO_2 is a reddish-brown gas with a typical odour. *It is poisonous*! Its dimer—N_2O_4—is a colourless easily compressible gas. These two compounds exist in equilibrium with each other at temperatures from −11.2 to 140 °C:

$$2NO_2 \underset{+140\,^\circ C}{\overset{-11.2\,^\circ C}{\rightleftarrows}} N_2O_4$$

The NO_2 molecule has an angular shape:



Nitrogen dioxide has a high chemical activity. The presence of a positive charge on the nitrogen atom underlies the oxidizing properties of NO_2, which manifests itself very clearly in disproportionation reactions. The dissolution of NO_2 in water is attended by the formation of HNO_2 and HNO_3:

$$2\overset{+4}{N}O_2 + H_2O = H\overset{+5}{N}O_3 + H\overset{+3}{N}O_2$$

Reactions with alkalies yield nitrates and nitrites:

$$2NO_2 + 2NaOH = NaNO_3 + NaNO_2 + H_2O$$

The dissolution of NO_2 in the presence of an excess of oxygen is attended by the formation of nitric acid:

$$4NO_2 + O_2 + 2H_2O = 4HNO_3$$

This reaction is used to produce nitric acid on a commercial scale.

In a laboratory, NO_2 is prepared by reacting copper with concentrated HNO_3:

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

Dinitrogen pentoxide N_2O_5 is obtained by the reaction of dehydration of nitric acid by diphosphorus pentoxide:

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5$$

Dinitrogen pentoxide forms colourless transparent crystals melting at 30 °C. Already at room temperature, it decomposes irreversibly into nitrogen dioxide and oxygen:

$$2N_2O_5 = 4NO_2\uparrow + O_2\uparrow$$

Dinitrogen pentoxide is a strong oxidizing agent. Many compounds burn readily in an atmosphere of N_2O_5. It reacts with water to form nitric acid:

$$N_2O_5 + H_2O = 2HNO_3$$

Questions and Problems

1. Compile the formulas of the equilibrium constant for the reactions:
(a) $NO_2 + NO \rightleftarrows N_2O_3$
(b) $2HNO_2 \rightleftarrows H_2O + N_2O_3$
Propose specific ways of shifting equilibrium (a) to the left; and (b) to the right.

2. Write out the equations of oxidation-reduction reactions from the text of this section and explain their balancing by the electron balance and ion-electron methods.

3. Prove that the properties of nitrogen dioxide are of an acidic nature.

4. Compare the properties of nitrogen dioxide and sulphur dioxide as acid oxides and explain their similarity and differences.

5*. A mixture of copper and copper(II) oxide was treated with concentrated nitric acid. The evolved gas occupied a volume of 1.12 lit. The solution after complete dissolution of the mixture was evaporated until dry, and then roasted. The mass of the residue was 4 g. What are the composition in per cent and the mass of the initial mixture?

6*. A commercial preparation of copper with a mass of 5 g was treated with nitric acid, and then the solution was evaporated and roasted to a constant mass, which was 4 g. Determine the content of the copper in the preparation in per cent by mass.

11.6. Nitric Acid

In a laboratory, nitric acid can be prepared by reacting concentrated sulphuric acid with nitrates:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

Nitric acid is produced commercially by the catalytic oxidation of ammonia by the oxygen of the air. This method consists of several steps. First, the mixture of ammonia and air is passed over a platinum catalyst at 800 °C. The ammonia is oxidized to nitrogen monoxide:

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

Cooling is attended by the further oxidation of the NO to NO_2:

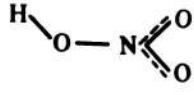
$$2NO + O_2 = 2NO_2$$

The formed nitrogen dioxide dissolves in water in the presence of a surplus of O_2 with the formation of HNO_3:

$$4NO_2 + O_2 + 2H_2O = 4HNO_3$$

Physical Properties. Pure nitric acid is a colourless liquid freezing at −42 °C. It fumes in air because its vapour forms minute droplets of mist with the moisture in the air. It mixes with water in any proportions.

Chemical Properties. Nitric acid is one of the strongest acids. In aqueous solutions, it dissociates completely into the ions H^+ and NO_3^-. It exhibits all the properties of acids. The HNO_3 molecule has a planar structure. The valence of the nitrogen in HNO_3 is four:



Nitric acid has only oxidizing properties. The nitrogen in the acid is in the highest oxidation state of nitrogen, +5. It can only gain electrons by exhibiting oxidizing properties. The action of light causes nitric acid to decompose:

$$4HNO_3 = 4NO_2 + O_2 + 2H_2O$$

The reduction of nitric acid depends on its concentration and the nature of the reducing agent. The oxidation state of nitrogen in the products of reduction ranges from +4 to −3, which corresponds to the scheme:

$$\overset{+5}{H}\overset{+5}{N}O_3 \rightarrow \overset{+4}{N}O_2 \rightarrow \overset{+3}{N}_2O_3 \rightarrow \overset{+2}{N}O \rightarrow \overset{+1}{N}_2O \rightarrow \overset{0}{N}_2 \rightarrow \overset{-3}{N}H_4\overset{+5}{N}O_3$$

Concentrated nitric acid oxidizes most metals (except for gold and platinum).

When concentrated nitric acid reacts with metals having a low activity, the product is generally NO_2:

$$Cu + 4HNO_3(conc.) = Cu(NO_3)_2 + 2\overset{+4}{N}O_2 + 2H_2O$$

Dilute nitric acid, on the other hand, is reduced to NO:

$$3Cu + 8HNO_3(dil.) = 3Cu(NO_3)_2 + 2\overset{+2}{N}O\uparrow + 4H_2O$$

If more active metals enter into a reaction with the acid, N_2O evolves*:

$$4Mg + 10HNO_3(dil.) = 4Mg(NO_3)_2 + \overset{+1}{N}_2O + 5H_2O$$

When very dilute nitric acid is reacted with active metals, it is reduced to ammonium salts:

$$4Zn + 10HNO_3(very\ dil.) \rightarrow 4Zn(NO_3)_2 + \overset{-3}{N}H_4\overset{+5}{N}O_3 + 3H_2O$$

Iron reacts readily with dilute nitric acid, but does not react in the cold with concentrated acid. Chromium and aluminium behave in a similar way. This is explained by the formation of oxide films on the surface of the metals that inhibit further oxidation. This phenomenon is called **passivation of a metal.**

Non-metals are oxidized to the relevant acids, while nitric acid depending on its concentration is reduced to NO or NO_2:

$$S + 6HNO_3(conc.) = H_2SO_4 + 6NO_2 + 2H_2O$$

$$P + 5HNO_3(conc.) = H_3PO_4 + 5NO_2 + H_2O$$

$$I_2 + 10HNO_3(conc.) = 2HIO_3 + 10NO_2 + 4H_2O$$

$$3P + 5HNO_3(dil.) + 2H_2O = 3H_3PO_4 + 5NO$$

* The products of the reaction of magnesium with nitric acid contain molecular hydrogen in addition to N_2O. The Soviet chemists A. Grinberg and A. Vyugina have proved that if magnesium and 10% nitric acid are taken in equivalent proportions, 120 ml of hydrogen evolve per gramme of metal. It had been shown earlier that when 25% HNO_3 is reacted with manganese, a gas mixture forms that contains 40% (by volume) of H_2, 39% of NO, 20% of N_2O, and traces of NO_2. Hence, the cited reactions of nitric acid with metals only indicate the nature of reduction of the nitrogen in its +5 oxidation state.

A mixture consisting of one volume of nitric and three volumes of concentrated hydrochloric acid is called **aqua regia**. It is a stronger oxidizing agent and oxidizes the noble metals—gold and platinum.

The salts of nitric acid, called **nitrates**, are crystalline substances dissolving well in water. When heated, they decompose with the evolution of O_2. The nitrates of the alkali metals transform into the relevant nitrites:

$$2KNO_3 = 2KNO_2 + O_2\uparrow$$

The nitrates of metals to the right of copper in the electromotive series of the metals decompose with the formation of the free metals:

$$2AgNO_3 = 2Ag + 2NO_2\uparrow + O_2\uparrow$$

The nitrates of the other metals decompose to oxides:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2\uparrow + O_2\uparrow$$
$$2Pb(NO_3)_2 = 2PbO + 4NO_2\uparrow + O_2\uparrow$$

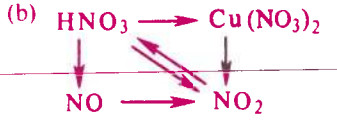
Application. Since nitrates contain nitrogen in its highest oxidation state and are therefore oxidizing agents, they are widely used for manufacturing readily flammable and explosive substances. For example, gunpowder is a mixture consisting of 68% of KNO_3, 15% of S, and 17% of C. Of the greatest importance are sodium nitrate $NaNO_3$, potassium nitrate KNO_3, calcium nitrate $Ca(NO_3)_2$, silver nitrate $AgNO_3$ (lapis), and ammonium nitrate NH_4NO_3.

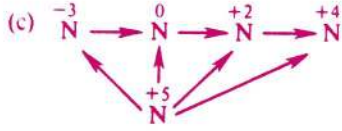
They are used very widely in agriculture as fertilizers.

Questions and Problems

1. Nitric acid is a typical acid. How is the typical nature of its properties expressed?
2. Compare nitric and sulphuric acids. What is the reason for the similarity of their properties?
3. How can the following transformations be performed:

(a) $N_2 \rightarrow NH_3 \rightarrow NO_2 \rightarrow HNO_3 \rightarrow Cu(NO_3)_2 \rightarrow CuO$;

(b) 

(c) 

(d) $NO_2 \rightarrow NO_3^- \rightarrow N_2 \rightarrow NO$?

4. Explain the hydrolysis of aluminium nitrate; support your answer with reaction equations.

5. Explain why nitric acid exhibits only oxidizing properties, while nitrous acid exhibits both oxidizing and reducing ones.

6[a]. The nitric acid used at laboratories contains 65% of HNO_3. What is the molar concentration of this acid? The density of the solution is 1.391 g/cm^3.

7[a]. What mass of 55% nitric acid can be produced from 15 tonnes of ammonia if the yield of the oxidation product is 98%, while the mass of the actual amount of acid produced is 94% of the theoretical value?

11.7. Phosphorus

Phosphorus is one of the abundant elements. Like carbon, hydrogen, and nitrogen, phosphorus is an essential constituent of all the living cells of animals and plants.

Phosphorus is not encountered in nature in the free state. It is contained in apatites $Ca_5X(PO_4)_3$, where X is fluorine (and more rarely chlorine or OH), and phosphorites $Ca_3(PO_4)_2$, which are the raw material for its production.

Phosphorus is obtained by a reaction proceeding at the temperature of an electric arc as follows:

$$5C + 3SiO_2 + Ca_3(PO_4)_2 = 5CO + 3CaSiO_3 + 2P$$

Physical Properties. Phosphorus forms three main allotropic modifications: white, red, and black. White phosphorus is the most chemically active of them. It self-ignites in the air and glows in the dark. Tetratomic molecules P_4 having the shape of a tetrahedron are stable in the liquid, dissolved state, and also in vapour below 1000 °C. It is obtained by rapidly cooling phosphorus vapour. *It is poisonous!*

Red phosphorus is prepared by the prolonged heating of white phosphorus without the access of air at 250-300 °C. It differs in its properties from white phosphorus—it is a dark red powder, is less active than white phosphorus, and is not poisonous.

Black phosphorus is obtained by heating white phosphorus at 200 °C under a high pressure. In its appearance, it reminds one of graphite, but unlike the latter is a semiconductor.

Chemical Properties. The oxygen compounds of phosphorus are more stable than those of nitrogen, whereas the hydrogen compound is less stable than ammonia. If NH_3 can be produced by direct synthesis from nitrogen and hydrogen, then PH_3 is produced indirectly. The chemical activity of phosphorus is considerably higher than that of nitrogen.

Unlike nitrogen, phosphorus is readily oxidized by oxygen. In an excess of oxygen, diphosphorus pentoxide forms, and in a deficit of it, diphosphorus trioxide:

$$4P + 5O_2 = 2P_2O_5$$
$$4P + 3O_2 = 2P_2O_3$$

Oxidation in the air is attended by glowing, i.e. **chemiluminescence** (the emission of light in chemical reactions) occurs.

The reaction of nitric acid with phosphorus yields phosphoric acid.

Halogens form trihalides or pentahalides with phosphorus:

$$2P + 3Cl_2 = 2PCl_3$$
$$PCl_3 + Cl_2 = PCl_5$$

Reactions of phosphorus with metals yield phosphides:

$$2P + 3Mg = Mg_3\overset{-3}{P}_2$$

Phosphorus under ordinary conditions does not react with hydrogen, therefore PH_3 is obtained either by reacting phosphorus with alkalies, or by reacting phosphides with water:

$$Ca_3P_2 + 6HOH = 3Ca(OH)_2 + 2PH_3$$

Phosphine PH_3 is a colourless gas soluble in water. *It is poisonous*! In a chemical respect, it reminds one of NH_3, although it differs from ammonia in a number of properties. When heated, phosphine decomposes into phosphorus and hydrogen. The reaction is reversible:

$$2PH_3 \rightleftarrows 2P + 3H_2$$

Phosphine forms phosphonium salts with acids:

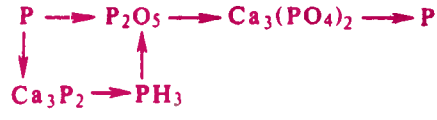
$$PH_3 + HX \rightarrow [PH_4]^+ + X^-$$

These salts form only with very strong anhydrous acids. The structure of the phosphonium cation $[PH_4]^+$ is similar to that of ammonium $[NH_4]^+$.

Questions and Problems

1. Indicate the similar and different properties of phosphorus and nitrogen.
2. How can the following transformations be conducted:

(a) $\overset{-3}{P} \rightarrow \overset{0}{P} \rightarrow \overset{+5}{P}$

(b)


3. Indicate the stable oxidation state of phosphorus and the compounds corresponding to it.
4. Can phosphine combine with HCl? What is the mechanism of this process, if possible, and what type of chemical bond forms?

11.8. Phosphorus Oxides. Phosphoric Acid

Phosphorus forms a number of oxides, of which diphosphorus pentoxide P_2O_5 and diphosphorus trioxide P_2O_3 have been studied the most and are important in a practical respect. There is also known the compound P_2O_4, which can be considered as a mixed oxide consisting of the two first named ones.

Diphosphorus trioxide P_2O_3 is formed when phosphorus burns in a limited amount of oxygen:

$$4P + 3O_2 = 2P_2O_3$$

It consists of white crystals and is polymorphous. It exists in several modifications built up from pyramidal structural units PO_3.

In its chemical properties, P_2O_3 is an acid oxide. It reacts with water to form phosphorous acid $H_2[PO_3H]$, and with alkalies to form the relevant salts:

$$P_2O_3 + 3H_2O = 2H_3PO_3$$

$$4NaOH + P_2O_3 = 2Na_2HPO_3 + H_2O$$

Diphosphorus trioxide has reducing properties; it is oxidized by oxygen to P_2O_5:

$$P_2O_3 + O_2 = P_2O_5$$

Diphosphorus pentoxide P_2O_5 is a snow-white powder that sublimes when heated. It absorbs water very actively and forms phosphoric acid:

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

This feature of P_2O_5 explains its widespread use as an effective dehydrating agent.

At low temperatures, P_2O_5 removes water from nitric acid:

$$P_2O_5 + 2HNO_3 = 2HPO_3 + N_2O_5$$

Being an acid oxide, it reacts with basic oxides and hydroxides:

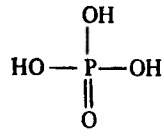
$$BaO + P_2O_5 = Ba(PO_3)_2$$

$$6NaOH + P_2O_5 = 2Na_3PO_4 + 3H_2O$$

Phosphoric acid H_3PO_4 (its common name is orthophosphoric acid) is the most important acid of phosphorus. It is prepared by reacting P_2O_5 with water. At a laboratory, this acid can be prepared by oxidizing phosphorus by a 30% HNO_3 solution:

$$3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO\uparrow$$

In phosphoric acid, all three hydrogen atoms are bound to oxygen atoms:



Anhydrous phosphoric acid forms white crystals readily soluble in water. In aqueous solutions, phosphoric acid is much weaker than sulphuric and nitric acids. It is a triatomic acid and dissociates in steps:

$$H_3PO_4 + H_2O \rightleftarrows H_3O^+ + H_2PO_4^- \quad \text{(1st step)}$$
$$H_2PO_4^- + H_2O \rightleftarrows H_3O^+ + HPO_4^{2-} \quad \text{(2nd step)}$$
$$HPO_4^{2-} + H_2O \rightleftarrows H_3O^+ + PO_4^{3-} \quad \text{(3rd step)}$$

Usually, the first step of dissociation predominates.

Phosphoric acid forms three kinds of salts—normal, hydrogen, and dihydrogen phosphates, e.g. Na_3PO_4, Na_2HPO_4, and NaH_2PO_4, respectively. Among these salts, only the phosphates of the alkali metals dissolve well in water.

The phosphorus in phosphoric acid is in its highest oxidation state, which is its stable form. This is why phosphoric acid is stable and unlike nitric and sulphuric acids has no appreciable oxidizing properties.

The salts of phosphoric acid are valuable mineral fertilizers. They include superphosphate, double superphosphate, precipitate, and ammophos.

Superphosphate is a mixture of $CaSO_4 \cdot 2H_2O$ with $Ca(H_2PO_4)_2$. It is produced by treating natural phosphorite with sulphuric acid:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaSO_4 + Ca(H_2PO_4)_2$$

Double superphosphate $Ca(H_2PO_4)_2$ is produced by reacting phosphoric acid with natural calcium phosphate:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$$

Precipitate $CaHPO_4 \cdot H_2O$ is insoluble in water, but dissolves in acid soils. Pure precipitate is used as a phosphorus-lime addition to cattle fodder. It is produced from calcium hydroxide:

$$Ca(OH)_2 + H_3PO_4 = CaHPO_4 \cdot 2H_2O$$

Ammophos—a mixture of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$—is a valuable fertilizer containing both nitrogen and phosphorus. It is produced by reacting ammonia with phosphoric acid.

Sodium dihydrogen phosphate NaH_2PO_4 is employed in medicine.

Organophosphorus compounds participate in the most important biochemical processes of an organism.

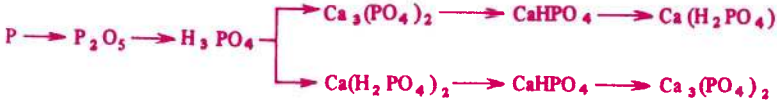
In the nucleic acids RNA and DNA, the mononucleotides are joined by residues of phosphoric acid. The nucleic acids RNA and DNA participate in protein synthesis, the transfer of hereditary features, and in other biochemical processes.

Questions and Problems

1. Diphosphorus pentoxide is an acid oxide. Describe its properties and support them with reaction equations.

2. Characterize phosphoric acid. How does its typical nature manifest itself? Give equations of the relevant reactions in the molecular and ionic forms.

3. How can the following transformations be conducted:



Write the reaction equations in the molecular and ionic forms. For an oxidation-reduction process, indicate the oxidizing and reducing agents.

4. Describe the hydrolysis of the salt Na_3PO_4 and indicate the required reaction equations.

5[a]. In 200 g of water there were dissolved 71 g of P_2O_5. What is the per cent concentration by mass of the phosphoric acid in the obtained solution?

6[a]. In 200 g of a 24.5% solution of H_3PO_4 there were dissolved 35.5 g of P_2O_5. What is the per cent concentration by mass of H_3PO_4 in the obtained solution?

7[a]. How many grammes of the starting material were used to produce 28.4 g of diphosphorus pentoxide if the phosphorus content in the starting material was 99.5%?

8[a]. When preparing a culture solution for plants, 2.5 g of KNO_3, 2.5 g of KH_2PO_4, and 10 g of $Ca(NO_3)_2$ were taken per litre of distilled water. What was the content of each of these substances in per cent by mass?

9[a]. The content of nutrient substances in phosphorus fertilizers is conditionally expressed in per cent by mass of diphosphorus pentoxide. Calculate the per cent by mass of P_2O_5 in the crystal hydrate $CaHPO_4 \cdot 2H_2O$.

SUMMARY

Nitrogen, phosphorus, arsenic, antimony, and bismuth form the main subgroup of Group V. The outer energy level of these elements has the electron configuration ns^2np^3, therefore in the ground state the elements of this subgroup have a valence of three.

Phosphorus, unlike nitrogen, has vacant *d* sublevels in its outer energy level.

Nitrogen and phosphorus form the hydrogen compounds RH_3 in the −3 oxidation state.

Nitrogen and phosphorus each contains two paired electrons in their hydrogen compounds. This structural feature determines the properties of NH_3 and PH_3 to attach an H^+ ion by the donor-acceptor mechanism.

Nitrogen and phosphorus form oxides in which the highest oxidation

state is +5. Nitric acid having exclusively oxidizing properties corresponds to dinitrogen pentoxide.

Phosphoric acid is a triatomic one and dissociates mainly in the first step.

Nitrogen and phosphorus compounds are used on a large scale as mineral fertilizers.

CHAPTER 12

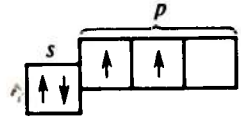
THE CARBON SUBGROUP

OBJECTIVES

To be able to characterize the features of the structure of atoms of the carbon subgroup elements and explain the differences between the elements of this subgroup proceeding from their structure; to know the structural features of the allotropic modifications of carbon and silicon and their most important oxygen compounds, and also the properties of carbonic and silicic acids and their salts.

12.1. General

Carbon, silicon, germanium, tin, and lead form Subgroup IVA. The outer energy levels of the Group IV *p* elements have four electrons (an s^2p^2 configuration) including two paired *s* electrons and two unpaired *p* electrons:



The electron configurations of these atoms are:

$_{6}C$—$1s^22s^22p^2$ (2nd period)

$_{14}Si$—$1s^22s^22p^63s^23p^2$ (3rd period)

$_{32}Ge$—$1s^22s^22p^63s^23p^63d^{10}4s^24p^2$ (4th period)

$_{50}Sn$—$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^2$ (5th period)

$_{82}Pb$—$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^2$ (6th period)

The energy level of carbon preceding the outer one contains two electrons, that of silicon—eight, and that of germanium, tin, and lead—18 electrons.

In the ground state, the elements of this subgroup exhibit a valence of two. In a transition to an excited state attended by the transfer of one of

the outer level *s* electrons into a free orbital of the *p* sublevel of the same level, all the electrons of the outer layer become unpaired, and the valence grows to four. For example,



Outer electron shell of carbon atom in ground state

Outer electron shell of carbon atom in excited state

The energy spent on the transfer of an electron is more than compensated by the energy liberated in the formation of four bonds.

When going from carbon to lead, the radii of neutral atoms grow. The tendency of filling up the outer energy level to an octet weakens, and consequently, the non-metallic properties attenuate and the metallic ones grow from carbon to lead. Only carbon and silicon are non-metals.

Carbon occupies a central position in the periodic table of the elements between the electropositive and electronegative ones. The relative electronegativity (REN) of carbon (2.5) equals the arithmetical mean value of the REN of fluorine (4) and lithium (1). This indicates that the ability of losing or gaining electrons is expressed the same in carbon.

In addition to its ability of forming covalent bonds with other elements, carbon has an exclusive property, namely, its atoms can combine with one another in virtually an endless number, forming a diversity of chains.

All the elements of Subgroup IVA form hydrogen compounds of the RH_4 type whose stability rapidly diminishes in the series C, Si, Ge, Sn, and Pb.

The elements form oxides of the RO and RO_2 types.

Questions and Problems

1. Write examples of compounds of the Group IV elements in which they are in the +4 and −4 oxidation states. What is their valence in these compounds? Defend your answer.

2. Compare the electron configurations of the atoms of elements of the carbon and nitrogen subgroups. Why is the transition $s^2p^2 \rightarrow sp^3$ possible for carbon?

3. How can you explain, proceeding from the structure of an atom, that the non-metallic properties weaken and the metallic ones grow when going from carbon to lead?

12.2. Carbon

In an excited carbon atom, the single *s* and three *p* electrons do not exist in the "pure" form. Four hybrid orbitals correspond to them that are identical in shape and are symmetrically directed in space at an angle of 109.5°.

Carbon can exhibit oxidation states of +4, +2, and −4.

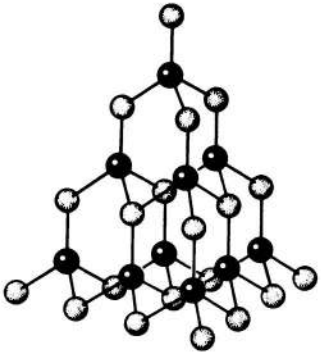


Fig. 28
Structure of a diamond crystal (the length of all the C—C bonds is 0.154 nm)

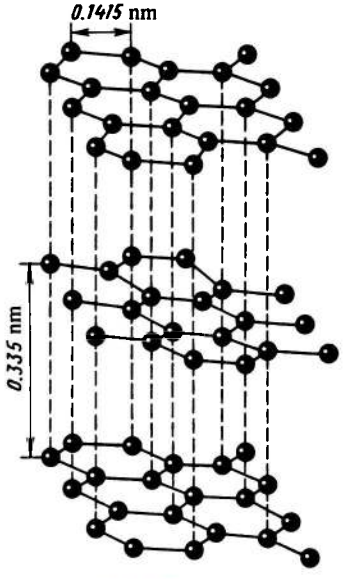


Fig. 29
Structure of graphite

Carbon atoms can form polymer structures of the coordination, lamellar, and linear type which the sp^3, sp^2, and sp hybrid states correspond to, respectively.

Physical Properties. Carbon forms three allotropic modifications—diamond, graphite, and carbyne.

Diamond is a colourless transparent substance that does not conduct an electric current. It has a cubic elementary cell (Fig. 28). Each carbon atom is surrounded by a regular tetrahedron consisting of four other atoms since sp^3 hybridization occurs. All the atoms in the crystal lattice are at an identical distance of 0.154 nm from one another, and each of them forms localized two-electron bonds with the neighbouring atoms. This structure explains the exceedingly high hardness of diamond.

Graphite is a dark gray opaque soft substance with a slight metallic lustre that conducts an electric current poorly. The crystal lattice of graphite, whose structure is shown in Fig. 29, differs substantially from diamond: it consists of infinite flat parallel layers formed of six-membered rings (hexagons). The length of a C—C bond in a hexagon is 0.1415 nm. The layers are spaced at a distance of 0.335 nm and are bound comparatively weakly to one another, which enables them to readily separate. This is just what explains the low mechanical strength of graphite.

Carbyne—a third allotropic modification of carbon—is a linear polymer. The carbon atoms in carbyne are joined by alternating triple and single bonds:

$$-C\equiv C-C\equiv C-C\equiv C-$$

Another polymer form is known, namely, polycumulene in which all the carbon atoms are joined by double bonds:

$$=C=C=C=C=C=$$

Chemical Properties. In a chemical respect, carbon is inert under normal conditions. Its reactivity grows with elevation of the temperature. For instance, when heated, carbon vigorously reacts with oxygen to form carbon monoxide or carbon dioxide, which depends on the amount of oxygen available:

$$2C + O_2 = 2CO$$
$$C + O_2 = CO_2$$

At high temperatures, carbon can also react with metals to form carbides:

$$Ca + 2C \longrightarrow Ca\begin{matrix}\diagup C \\ \| \\ \diagdown C\end{matrix}$$ Calcium carbide

At the temperature of an electric arc, carbon combines with hydrogen to form methane:

$$C + 2H_2 \rightarrow CH_4$$

When steam is passed over red hot coal or coke, a mixture of carbon monoxide and hydrogen called **water gas** is obtained:

$$C + H_2O = CO + H_2$$

This reaction proceeds in a gas generator at a temperature above 1200 °C. Below 1000 °C, the carbon is oxidized to CO_2:

$$C + 2H_2O = CO_2 + 2H_2$$

The conversion method of producing hydrogen is based on these two reactions.

Carbon can reduce many metals from their oxides. This underlies the production of metals from their ores.

Concentrated sulphuric and nitric acids when heated oxidize carbon to CO_2:

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$
$$3C + 4HNO_3 = 3CO_2 + 4NO + 2H_2O$$

Questions and Problems

1. Indicate the oxidation state and valence of carbon in the free state.
2. Compile the equations of the reactions of formation of calcium carbide and water gas, and of the reaction of carbon with nitric and sulphuric acids.
3. The transition of a carbon atom to the excited state ($1s^2 2s^2 2p^2 \rightarrow 1s^2 2s^1 2p^3$) is attended by the absorption of energy. Why are all the bonds in CH_4 equivalent in this case?

12.3. Carbon Oxides

Carbon monoxide CO. In a molecule of this oxide, the carbon atom is in the ground state. It forms two bonds with an oxygen atom at the expense of the two *p* electrons. The third bond forms by the donor-acceptor mechanism, the oxygen being a donor of an electron pair which the carbon atom accepts in the free $2p$ orbital.

The interatomic distance is 0.113 nm. Therefore, carbon monoxide has the following structural formula:

$$:C \equiv O:$$

Carbon monoxide is a colourless odourless gas very sparingly soluble in water. *It is poisonous*! Its poisoning effect consists in it reacting irreversibly with the haemoglobin of the blood, owing to which the transfer of oxygen from the lungs to tissues stops.

Carbon monoxide is a chemically inert compound. When the temperature is elevated to 200 °C and the pressure is 15×10^5 Pa, carbon monoxide reacts with NaOH to form the sodium salt of formic acid:

$$CO + NaOH \longrightarrow HC\begin{matrix}=O\\ \diagdown ONa\end{matrix}$$

Carbon monoxide is oxidized to the dioxide at 700 °C:

$$2CO + O_2 = 2CO_2\uparrow$$

Its reaction with water vapour forms CO_2 and H_2:

$$CO + H_2O \rightarrow CO_2\uparrow + H_2\uparrow$$

Carbon monoxide is a vigorous reducing agent. It reduces many metals from their oxides, which is employed in metallurgy when producing metals from their ores:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2\uparrow$$

Carbon dioxide CO_2 has a linear structure. The bonds in the molecule are formed at the expense of four electron pairs:

$$\ddot{O} = C = \ddot{O}$$

Each of the carbon-oxygen bonds is polar, therefore there should be a certain negative charge on each of the oxygen atoms, and a positive charge concentrated on the carbon atom. Since the oxygen atoms are on one straight line at both sides of the carbon atom and at equal distances from it, the centres of distribution of the positive and negative charges coincide. Consequently, the charge on the carbon is completely neutralized. Hence, although each of the carbon-oxygen bonds is polar, the CO_2 molecule as a whole is non-polar, and its linear structure is responsible for this.

Carbon dioxide forms in the thermal decomposition of carbonates. It is produced commercially by roasting limestone:

$$CaCO_3 = CaO + CO_2$$

It can be prepared in a laboratory by reacting dilute acids with carbonates:

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

Under conventional conditions, CO_2 is a colourless gas 1.5 times heavier than air. It is soluble in water (at 0 °C one litre of water dissolves 1.7 litres of carbon dioxide).

With elevation of the temperature, the solubility of CO_2 greatly diminishes, and its excess evolves from a solution in the form of bubbles producing a foam. This property is used to produce effervescent drinks.

When greatly cooled, CO_2 crystallizes in the form of a white snowlike mass that when compressed evaporates very slowly, lowering the temperature of its surroundings. This explains its use as "dry ice". It does not support respiration, but is a source of nutrition for green plants (photosynthesis).

The property of CO_2 consisting in its failure to support burning is used in fire extinguishing equipment.

At high temperatures, carbon dioxide can react with metals whose affinity to oxygen is higher than in carbon itself (e.g., with magnesium):

$$CO_2 + 2Mg = 2MgO + C$$

When CO_2 is dissolved in water, a partial reaction of these substances occurs leading to the formation of carbonic acid H_2CO_3.

Questions and Problems

1. What are the valence and oxidation state of carbon and oxygen in CO?
2. Compile equations of reactions typical of CO_2 as an acid oxide.
3. How can the following transformations be conducted?



4*. How much heat is evolved in the combustion of 2 g of coal? The thermochemical equation of the reaction is:

$$C + O_2 = CO_2; \quad \Delta H = -393.5 \text{ kJ}$$

5. How many litres of CO_2 can be produced from 600 kg of limestone containing 30% of impurities?

6*. The carbon dioxide obtained in the decomposition of 12.5 g of limestone was passed into a solution containing 5 g of calcium hydroxide. What salt and how many grammes of it were obtained if the limestone contained 80% of $CaCO_3$ by mass?

7*. A mixture of CO and CO_2 with a mass of 10 g occupies a volume of 6.72 lit. Determine the composition of the mixture in per cent by volume.

8*. A mixture of CO and CO_2 occupying a volume of 8.96 lit was mixed with oxygen and exploded. The volume of the gases diminished by 3.36 ml. What was the composition of the initial mixture in per cent by volume?

9*. A mixture of CO and CO_2 has a relative density with respect to hydrogen of 16. What is the composition of the mixture in per cent by volume?

10*. A mixture of CO and CO_2 with a volume of one litre was passed through 50 g of a 3.32% solution of potassium hydroxide. An acid salt formed. What was the composition of the mixture in per cent by volume?

12.4. Carbonic Acid and Its Salts

Carbonic acid is very weak, it exists only in aqueous solutions, and dissociates insignificantly into ions. This is why aqueous solutions of CO_2 have weakly acidic properties:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$$

The structural formula of carbonic acid is $HO - \overset{\overset{O}{\|}}{C} - OH$. It is a diatomic acid and forms two types of salts, namely, normal salts—**carbonates**, and acid salts—**hydrogen carbonates**. Only Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3 and $(NH_4)_2CO_3$ are soluble, whereas the hydrogen carbonates dissolve readily in water, except for $NaHCO_3$.

The carbonates and hydrogen carbonates can be prepared by reacting CO_2 with solutions of bases or by exchange reactions:

$$NaOH + CO_2 = NaHCO_3$$

$$KHCO_3 + KOH = K_2CO_3 + H_2O$$

$$BaCl_2 + Na_2CO_3 = BaCO_3\downarrow + 2NaCl$$

When heated strongly, the alkali metal carbonates melt without decomposing, while the other carbonates when heated readily decompose into the oxide of the relevant metal and CO_2:

$$CaCO_3 = CaO + CO_2$$

Hydrogen carbonates when heated transform into carbonates:

$$2NaHCO_3 = Na_2CO_3 + CO_2\uparrow + H_2O$$

The alkali metal carbonates in aqueous solutions have a strongly alkaline reaction owing to hydrolysis:

$$Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + NaOH$$

The carbonate ion CO_3^{2-} and hydrogen carbonate ion HCO_3^- can be identified qualitatively by a reaction with stronger acids. The evolution of carbon dioxide with its typical "boiling" indicates the presence of these ions.

By passing the evolved CO_2 through lime water, one can observe turbidity of the solution due to the formation of calcium carbonate:

$$CaCO_3 + 2HCl = CaCl_2 + CO_2\uparrow + H_2O$$
$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$

When the CO_2 is passed through the solution for a long time, the latter again becomes transparent owing to the formation of the hydrogen carbonate:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

The anion of the soluble salts becomes hydrolyzed.

The following salts of carbonic acid are of a major significance:

Calcium carbonate $CaCO_3$; it occurs in nature in the form of the mineral calcite and is an important constituent of chalk, marble, and limestone.

Sodium carbonate $Na_2CO_3 \cdot 10H_2O$; it is a very important product of the basic chemical industry and is employed in virtually all the spheres of chemical production. The anhydrous salt is called calcined soda.

Potassium carbonate K_2CO_3, or potash; it is used in the production of refractory glass.

Sodium hydrogen carbonate $NaHCO_3$ (sodium bicarbonate); it is used in cookery, in medicine, and in the production of baking powder.

Questions and Problems

1. Explain from the standpoint of the theory of chemical equilibrium why the hydration of CO_2 is facilitated at pH > 8.

2. How can Na_2CO_3 be produced in different ways? Explain your answer.

3. Explain the hydrolysis of Rb_2CO_3. Is the reaction of the solution acidic or basic when this salt is dissolved?

4*. When potassium carbonate reacts with 14 g of 29.57% HCl, there were evolved 2.2 g of CO_2. How many grammes of K_2CO_3 entered into the reaction? Was the acid completely used up?

5*. A specimen of sodium carbonate with a mass of 10 g was dissolved in water, and 20 g of a 49% sulphuric acid solution were added. The solution was heated up to the complete evolution of CO_2, and the excess acid was neutralized with 56 g of a 5% KOH solution. What was the content of Na_2CO_3 in the specimen in per cent by mass?

6[a]. A mixture of magnesium and calcium carbonates with a mass of 14.2 g was treated with an excess of sulphuric acid. The mass of the evolved CO_2 was 6.6 g. What amount of calcium was contained in the mixture in per cent by mass?

7[a]. An excess of a sodium carbonate solution was added to 50 ml of a calcium chloride solution. The precipitate was filtered off, dried, and roasted. The mass of the residue was 1.4 g. What was the content of $CaCl_2$ in the initial solution in per cent by mass?

8[a]. A mixture of sodium carbonate and hydrogen carbonate with a mass of 19 g was heated until the gas stopped evolving. The mass of the residue was 15.9 g. Find the composition of the mixture in per cent by mass.

12.5. Silicon

Silicon is an analogue of carbon, but its non-metallic properties are weaker than those of carbon.

The sp^3 hybrid state is more typical of silicon, therefore it exhibits oxidation states of +4 and −4 in its compounds.

Silicon occurs in nature in the form of its oxide SiO_2, also known as **silica**, which is encountered as sand and quartz. **Silicates**—derivatives of silicic acid—are another group of natural silicon compounds. The most widespread are aluminosilicates that include soda feldspar (albite) $NaAlSi_3O_8$, common potash feldspar (orthoclase) $KAlSi_3O_8$, clay (kaolin) $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$, and nepheline $NaAlSiO_4$.

Silicon is prepared by reducing SiO_2 by magnesium:

$$SiO_2 + 2Mg = 2MgO + Si$$

or $SiCl_4$ by zinc:

$$SiCl_4 + 2Zn = Si + 2ZnCl_2$$

Properties of Silicon and Its Compounds. Silicon forms two allotropic modifications. In accordance with the sp^3 hybridization, the diamond-like (cubic) modification is the most stable one of silicon. The crystals of this modification have a dark gray metallic lustre and conduct an electric current. Amorphous silicon is a brown powder.

Crystalline silicon is chemically comparatively inert, while the amorphous modification is more reactive.

Silicon reacts only with strong oxidizing and reducing agents. It reacts with fluorine under ordinary conditions, and with oxygen and chlorine at 400-600 °C:

$$Si + 2F_2 = SiF_4$$

$$Si + O_2 = SiO_2$$

$$Si + 2Cl_2 = SiCl_4$$

At very high temperatures, silicon can combine directly with carbon and nitrogen:

$$Si + C = SiC$$

$$3Si + 2N_2 = Si_3N_4$$

Alkalies oxidize silicon to salts of silicic acid. Hydrogen also evolves in these reactions:

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2\uparrow$$

Silicon reacts with water (steam) at high temperatures:

$$Si + 3H_2O(g) = H_2SiO_3 + 2H_2\uparrow$$

Silicon dissolves in many metals. With some of them—Sn, Al, Zn, Pb, Au, and Ag—it does not react chemically. With other metals such as Mg, Ca, Cu, Fe, Pt, and Bi it reacts with the formation of silicides:

$$2Ca + Si = Ca_2Si$$

Silicon Dioxide and Silicic Acid. Of the several modifications of silicon dioxide SiO_2 occurring abundantly in nature, **quartz** is of the greatest significance. It forms quartz sands, veined quartz, sandstones, and is also contained in many species of rock (granites, etc.).

Silicon dioxide is practically insoluble in water because it has an atomic crystal lattice; as an acid oxide, it reacts with alkalies when heated to form silicates—salts of silicic acid:

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$$

Silicon dioxide can displace CO_2 from carbonates:

$$SiO_2 + Na_2CO_3 \overset{\text{fusion}}{=} Na_2SiO_3 + CO_2$$

Silicon carbide SiC called **carborundum** is prepared by heating a mixture of SiO_2 with carbon to 2000 °C:

$$SiO_2 + 3C = SiC + 2CO$$

Silicon dioxide reacts with hydrofluoric acid:

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

Silicon dioxide is widely used in the silicate industry in the manufacture of glass, ceramics, concrete articles, silicate brick, and so on.

Weak silicic acids combined by the general formula $nSiO_2 \cdot mH_2O$ correspond to silicon dioxide. **Orthosilicic H_4SiO_4, metasilicic** (or silicic) H_2SiO_3 and some other acids have been obtained in the free state.

When an aqueous solution of sodium silicate is acidified, free silicic acid separates:

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$

In the freshly cooled state, it is a gelatinous substance corresponding to the formula $(H_2SiO_3)_x$.

Silicic acid is thermally unstable and when heated readily decomposes into SiO_2 and water:

$$H_2SiO_3 = H_2O + SiO_2$$

Silicic acid is weaker than carbonic acid:

$$Na_2SiO_3 + H_2O + CO_2 = Na_2CO_3 + H_2SiO_3$$

The silicates soluble in water have an alkaline reaction in aqueous solutions, which is due to their hydrolytic decomposition with the formation of salts of polysilicic acids:

$$2Na_2SiO_3 + HOH \rightleftarrows Na_2Si_2O_5 + 2NaOH$$

Silicic acid cannot be prepared in the free state. In aqueous solutions, it forms a colloidal solution or a sol that exists for a very short time. The sol further coagulates and forms a gel. When the latter is dried, products with a porous structure called silica gels form that are used as drying agents and adsorbents.

The silicates are insoluble in water except for sodium and potassium silicates.

Aqueous solutions of Na_2SiO_3 and K_2SiO_3 are called **liquid** or **water glass** and are used to fabricate acid-resistant cement and concrete. Amorphous alloys—glasses—are obtained when mixtures of many silicates are heated with silicon dioxide.

Of great importance among the aluminosilicates are the **zeolites**. Their composition is expressed by the general formula $M_xE_yO_{2y}\cdot H_2O$, where M is Ca, Na (more rarely Ba, Sr, and K), E is Si and Al in a variable proportion.

Zeolites can exchange water for other substances (NH_3, ethanol, etc.), therefore they are used as what are called molecular sieves. The latter absorb substances whose molecules can enter their spaces. This property is widely employed for separating gaseous substances, and for drying gases and liquids. In zeolites, some cations can be replaced by others, therefore they are used as cation exchangers.

Pure silicon is one of the most important semiconductors. It is used in the radio and electronic industry. Silicon photoelectric cells can transform solar energy into electrical energy, which is of major significance for spaceships.

Questions and Problems

1. Why are the non-metallic properties of silicon less pronounced than in carbon?
2. Explain the similarities and differences in the properties of CO_2 and SiO_2, H_2CO_3 and H_2SiO_3.

3[a]. In the combustion of 6.2 g of silicon hydride, 12 g of SiO_2 were obtained. The density of the initial substance relative to air was 2.14. Determine the true formula of silicon hydride.

4[a]. How many grammes of silicon containing 10% of impurities entered into a reaction with sodium hydroxide if 3.36 lit of hydrogen evolved?

SUMMARY

Subgroup IVA includes carbon, silicon, germanium, tin, and lead. The electron configuration of the outer energy level ns^2np^2 indicates the presence of a free orbital in the $2p$ sublevel. This is why these elements can exhibit a valence of two and four. Down the subgroup from carbon to lead, the atomic radii increase and the electron affinity diminishes; the non-metallic properties attenuate, and the metallic ones grow. Carbon forms two stable oxides: CO and CO_2. The weak diatomic carbonic acid H_2CO_3 existing only in aqueous solutions corresponds to carbon dioxide. The acid forms two types of salts—carbonates and hydrogen carbonates. The most stable oxide of silicon is SiO_2 with a high chemical inertness. Silicic acid H_2SiO_3 corresponding to this oxide is weaker than carbonic acid.

CHAPTER 13

THE NOBLE GASES. SUMMARY OF THE PROPERTIES OF THE NON-METALS

OBJECTIVES

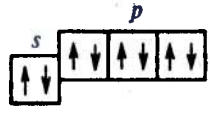
To characterize the features of the structure of the noble gas atoms; to explain the laws of the changes in the properties of the noble gases and the relation between the non-metals within the periods and groups.

13.1. The Noble Gases

The main subgroup of Group VIII is represented by helium He, neon Ne, argon Ar, krypton Kr, xenon Xe, and radon Rn. Every period terminates in one of these elements, therefore their atoms are distinguished by the maximum filling up of the outer energy levels:

$_{2}He—1s^2$ (1st period)
$_{10}Ne—1s^22s^22p^6$ (2nd period)
$_{18}Ar—1s^22s^22p^63s^23p^6$ (3rd period)
$_{36}Kr—1s^22s^22p^63s^23p^63d^{10}4s^24p^6$ (4th period)
$_{54}Xe—1s^22s^22p^63s^23p^63d^{10}4s^24p^65d^{10}5s^25p^6$ (5th period)
$_{86}Rn—1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^6$ (6th period)

The shell of helium consists of only two electrons. The other elements have eight electrons in their outer levels. The configuration of the outer energy levels of neon, argon, krypton, xenon, and radon is expressed by the formula s^2p^6:

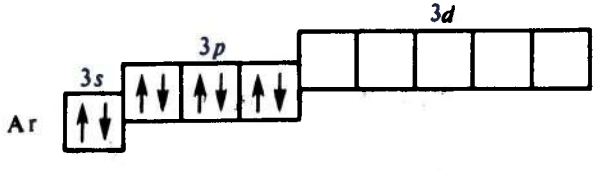


The absence of unpaired electrons points to the impossibility of forming compounds at the expense of a covalent bond, hence the molecules of the simple substances formed by these elements are monatomic. The features of the structure of these elements and their high chemical inertness have determined their group name—the **noble gases.**

Helium is the most inert of all the chemical elements. The orbitals of its electrons are absolutely identical and are at the minimum possible distance from the nucleus.

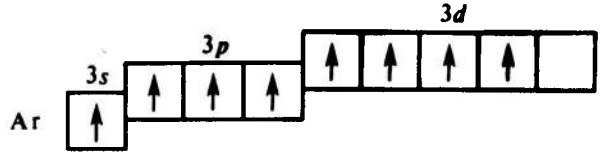
Neon has a filled electron shell. Its two electron levels accommodate two and eight electrons, respectively. It is in the second period and has an exceedingly high chemical inertness. In this respect, it is comparable with helium.

Argon, krypton, xenon, and radon are in the third, fourth, fifth, and sixth periods, respectively, and, consequently, in addition to the filled up *s* and *p* sublevels, these atoms have vacant orbitals of the *d* sublevels. Let us consider argon as an example:



The presence of vacant orbitals in the sublevels of the same level indicates the possibility of an atom passing over from its ground state to an excited one with the formation of the relevant number of unpaired elec-

trons. This is why the following transition is possible for argon (and also for Kr, Xe, and Rn):



The possibility of the transition of noble gas atoms to an excited state allows some of their compounds to be obtained. This shows that their chemical inertness is relative. Xenon fluorides XeF_2, XeF_4, and XeF_6 have been prepared, for example. The hexafluoride is quite active chemically and exhibits oxidizing properties. Xenon oxides XeO_3, XeO_4, etc. are known. It is very difficult to obtain compounds of the noble gases, however, and under ordinary conditions they do not participate in chemical reactions. It is exactly the high inertness of the noble gases that determines the field of their application.

Helium owing to properties such as inertness, light mass, mobility, and high heat conductivity has found many applications. For instance, the pressing of flammable substances from one vessel into another is performed safely with the aid of helium.

A fundamental contribution to the investigation of the properties of liquid helium was made by the outstanding Soviet physicists, Nobel Prize winners L. Landau and P. Kapitsa.

Biological investigations have shown that a helium atmosphere does not affect the genetic apparatus of humans and does not affect the development of cells and the frequency of mutations. The breathing of helium air (air in which the nitrogen has been partly or completely replaced by helium) increases the metabolism of oxygen in the lungs and prevents nitrogen embolism (caisson disease).

Neon is often used in engineering instead of helium. It is widely employed for manufacturing neon-filled lamps.

Argon is more available than helium and neon. This gas is widely used in metallurgy. It is generally employed in the hot processing of titanium, niobium, hafnium, uranium, thorium, and alkali metals where any contact with oxygen, nitrogen, water, and carbon dioxide must be excluded. The method of shielded argon arc welding has come into great favour.

Krypton is mainly used in the production of electric lamps.

Xenon has found a major application in the production of xenon lamps characterized by a correct colour transmission. Xenon is an X-ray contrast substance widely used in the fluoroscopy of the brain.

Although radon is radioactive, in ultramicrodoses it has a positive effect on the central nervous system. This is why it is used in treating patients at health resorts and in physiotherapy (radon baths).

Questions and Problems

1. Xenon has vacant *d* orbitals in its outer energy level, into which electrons of the *p* sublevel of the same level can be excited. Proceeding from this circumstance, explain the valence of xenon in the normal and excited states, and also its oxidation state in the compounds XeF_4, XeF_6, $XeOF_4$, and XeO_4.

2. Xenon fluorides are strong oxidizing agents, which is witnessed by the reaction equation

$$XeF_4 + 4KI = 2I_2 + Xe + 4KF$$

Indicate the oxidation states of the atoms before and after the reaction, and also the electron transitions using the electron balance method.

13.2. Non-Metals in the Periodic Table

When studying the structure of the periodic table and the arrangement of the chemical elements in it, it is easy to note that the metallic elements are separated from the non-metals by a conditional diagonal line from boron to astatine. The non-metals occupy the upper right part of the table and are arranged by periods as follows: two elements (H and He) in the first period, six elements (B, C, N, O, F, Ne) in the second one, five elements (Si, P, S, Cl, Ar) in the third one, four (As, Se, Br, Kr) in the fourth period, three elements (Te, I, Xe) in the fifth one, and two (At, Rn) in the sixth one.

A feature of the non-metals is that in their atoms the building up of the outer electron shells is close to the maximum, while the atomic radii tend to a minimum (across each period from left to right). When a non-metal is farther to the right of a period, its ionization energy and electron affinity are higher. This is why the atoms of the non-metals exhibit a tendency of forming an electron shell with the configuration of a noble gas. This is realized by an ability to gain electrons that grows across a period. Within the groups, this law manifests itself up them, therefore fluorine is the most electronegative element.

In non-metals, the oxidation state in their hydrogen compounds can be determined from the difference $(G - 8)$, where G is the number of the group containing the given non-metal. Consequently, every atom of a non-metal can combine with $(8 - G)$ hydrogen atoms. For example, one carbon atom (Group IV) can combine with four hydrogen atoms because the oxidation state of carbon is $4 - 8 = -4$. The highest positive oxidation state of the non-metals is usually $+G$. For instance, the oxidation state of chlorine in $HClO_4$ is $+7$.

Seven non-metallic elements exist in the form of diatomic molecules. Five of them at standard temperature and pressure are gases—hydrogen, nitrogen, oxygen, fluorine, and chlorine; bromine is a liquid, and iodine is a crystalline substance capable of subliming without melting.

The other non-metals at STP form crystals varying in their structure (e.g., carbon in the form of diamond) or are monatomic gases (the noble gases).

Most of the non-metals occur in nature in the form of compounds with other elements. Only oxygen, nitrogen, sulphur, carbon, and the noble gases are encountered in the form of simple substances.

In summarizing the physical properties of the non-metals, it should be stressed that they have no typical lustre and are coloured differently; in the crystalline state, they are distinguished by the structure and strength of the crystals; they are poor conductors of heat and electricity. The oxides of most non-metals are covalent compounds and in their chemical properties relate to acid oxides.

The non-metallic elements in nature are encountered mainly in the form of compounds, which is explained by their high chemical activity. The noble gases are encountered in the free state, and their simple substances are monatomic, which is associated with the features of the structure of their atoms.

The ways of obtaining the non-metallic elements in the form of simple substances are based primarily on their chemical activity. The common feature of these methods is that in the majority of cases they are based on oxidation-reduction reactions.

The reactivity of the non-metals varies within broad limits: for some of them it is only necessary that a reaction partner be present (for example, the reaction of halogens with metals), while for others special conditions must be observed including a high temperature, pressure, and sometimes a catalyst (e.g., nitrogen with hydrogen).

Questions and Problems

1. List the non-metallic elements, and indicate their position in the periodic table.
2. Why does the number of non-metallic elements in a period diminish down the periodic table? Defend your answer in accordance with the structure of an atom.
3. What laws are observed in the changes in the properties of the non-metals belonging to the third period?
4. How do the oxidizing properties of the non-metals change within a period and within a group? Defend your answer with specific examples.
5. Use the non-metals of the second period to explain the laws of the change in the structure of the outer electron shells.
6. Hydrogen belongs to the *s* elements, but in certain properties it is closer to the halogens. What properties do we have in view here and how is this related to the structure of hydrogen?

7. The atoms of the elements in a given subgroup are characterized by the same electron configuration of their outer shells, but the increase in their nuclear charge (atomic number) is attended by a change in their valence and oxidation-reduction properties. What causes these phenomena?

8. Why do the noble gases fail to form diatomic molecules?

9. Which of the molecules H_2S, HBr, H_2O, CO, and NH_3 are the most polar? Arrange them in the order of the decrease in their polarity.

10. Enumerate the most important physical properties of the non-metallic elements and explain them proceeding from the structure of their atoms.

11. The non-metals form hydrogen compounds of the general formula $EH_{(8-G)}$, where G is the group number. With this in view, write the formulas of the hydrogen compounds for the third-period non-metals, arrange them in the order of decreasing polarity, and characterize their acid properties.

12. Explain the structure of the hydrogen compounds of the nitrogen subgroup elements. Why does the neutral molecule RH_3 attach a proton? What kind of bond forms in this case and according to what mechanism?

13. The highest oxidation state is known to grow within a period with an increase in the atomic number. With this in view, write the formulas of the highest oxyacids of the third-period non-metals and compare their oxidizing properties.

14. Write the equations of the reactions illustrating the properties of dilute and concentrated sulphuric and nitric acids. Explain these properties.

15. Write the formulas of the possible oxides for the second-period non-metals and characterize their properties in the form of the relevant reaction equations.

16. What ions form in the dissociation of a molecule corresponding to the formula H_2O, $HClO_4$, H_3PO_4, HBr, or H_2S? What is the hydrogen ion from the viewpoint of atomic structure?

17. List the non-metals whose simple substances are diatomic molecules. Explain their structure and characterize their reactivity.

18. Name the allotropic modifications of the non-metals you know. Why do they differ from one another in their physical properties? Support your answer with appropriate examples.

19. An element whose highest salt-forming oxide has the formula E_2O_5 forms a hydrogen compound containing 3.85% of hydrogen. Name the element. Defend your answer with calculations.

20. Generally gaseous nitrogen is prepared at a laboratory by the thermal decomposition of ammonium nitrite. Determine the volume of the formed gaseous nitrogen measured at 22 °C and a pressure of 101.325 kPa if 3.26 g of NH_4NO_2 decomposed.

21. Explain why xenon forms a number of stable fluorides and why argon lacks such an ability.

22. Write the equations of the reactions of each of the following substances with water: diphosphorus pentoxide, lithium hydride, nitrogen dioxide, carbon dioxide, sulphur dioxide. What can you say about each of the formed compounds?

23. Write the formulas of each of the compounds listed below and indicate the oxidation state of the characteristic non-metal atoms: nitrous acid, iron(II) sulphide, potassium chlorate, sodium periodate, calcium phosphate, and sodium hydrogen carbonate.

24. Indicate any two chemical and two physical properties in which a given non-metal differs from a metal.

25. Is there a relation between the electronegativity of an element and its oxidation state? Use specific examples to defend your answer.

CHAPTER 14

A GENERAL REVIEW OF THE METALS

OBJECTIVES

To determine the position of the metals in the periodic table; to describe the features of the atomic structure of the metallic elements; to explain the features of the crystalline structure of the metals; to describe the nature of a metallic bond and its differences from an ordinary covalent or ionic bond; to compile equations of reactions characterizing the chemical properties of the metals; to describe the most important ways of producing metals.

14.1. Position in the Periodic Table and General Properties of the Metals

Over 80% of the known chemical elements are metals. In accordance with the structure of their electron shells, they include the *s* elements of Groups I and II, all the elements of the *d* and *f* families, the *p* elements of Group III (except boron), and also tin and lead (Group IV), bismuth (Group V), and polonium (Group VI). Most metals have from one to three electrons in their outer energy level. This explains their weak electronegativity in comparison with the non-metals.

The metal elements belonging to the *s* family form the main subgroups of Groups I and II, while those belonging to the *d* family form the secondary subgroups. In the *d* element atoms across a period, the *d* sublevels of the level preceding the outer one become filled by electrons.

Metals in whose atoms the *f* sublevels of the third level from the outer one are filled form the lanthanoid and actinoid families, each of which contains 14 elements.

Physical Properties. Metals have a crystalline structure in which three types of crystal lattices are encountered: cubic face-centred, hexagonal, and cubic body-centred (Fig. 30). They are close-packed structures. The electrons responsible for a metallic bond belong not to two individual atoms, but freely migrate over an entire crystal.

Electrical conductance, which is a most important physical property of the metallic state, occurs through the agency of these electrons. This is why metals are related to conductors of the first kind. If a potential difference is applied to a metal, the free electrons acquire directed motion and migrate from the negative pole to the positive one, i.e. a directed flow of moving electrons is set up—an electric current.

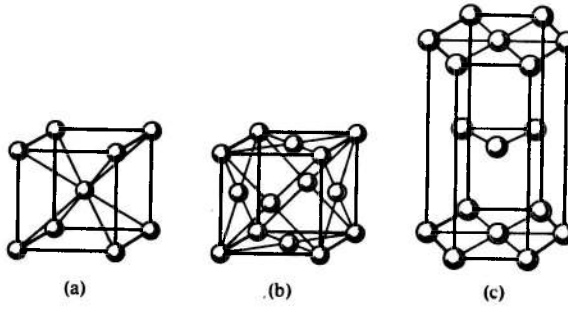


Fig. 30
Crystal lattices of metals:
a—cubic body-centred; *b*—cubic face-centred; *c*—hexagonal

The electrical conductance of metals depends greatly on the temperature. With elevation of the latter, the vibrations of the ions at the lattice points grow, and this, in turn, is a major hindrance to the directed motion of the electrons. When the temperature is lowered, the thermal vibrations of the ions at the lattice points greatly diminish, and the electrical conductance grows. At temperatures close to absolute zero, superconductance appears in most metals.

The thermal conductance of metals is also associated with the mobility of the free electrons and the vibration of the atoms themselves. These vibrations propagate in the form of a system of elastic (heat) waves along the entire crystal lattice. The free electrons collide with the vibrating atoms and exchange energy with them. This is why when a metal is heated, the heat energy is immediately transmitted from atom to atom owing to the free electrons. The temperature comparatively rapidly levels out throughout the entire mass of the metal.

All metals except mercury are solids. Mercury is the only metal that is liquid under ordinary conditions—its melting point is $-39\,^{\circ}C$. Most metals range in colour from dark gray to silver white. In engineering, ferrous and non-ferrous metals are distinguished.

The ferrous metals include iron and all its alloys, all other metals being non-ferrous ones. Sometimes the noble metals—gold and the platinum metals, are singled out into a separate group.

With respect to their density, light and heavy metals are distinguished. Metals with a density below 5 g/cm^3 are considered to be light, and with a density above this value—heavy.

With respect to their melting point, metals are divided into low-melting (a melting point below $1000\,^{\circ}C$) and refractory (a melting point above $1500\,^{\circ}C$) ones. The main mechanical properties include **elasticity**—the

property of reducing the initial shape after removal of the deforming forces, and **plasticity**—the state of a metal in which it is capable of retaining a change in its shape caused by the effect of deforming forces after their action has stopped.

Chemical Properties. These properties of metals are due to the typical structure of their outer electron shells.

We have already indicated that the atomic radii decrease across a period when the number of electron shells does not change. The alkali metal atoms have the largest radii. When the radius of an atom is smaller, its ionization energy is higher, and vice versa. Since metal atoms have the largest atomic radii, they have comparatively low values of the ionization energy and electron affinity, as a whole.

Free metals exhibit reducing properties exclusively.

The metals form oxides M_xO_y. For example:

$$4Na + O_2 = 2Na_2O \qquad 2Fe + O_2 = 2FeO$$

With the halogens, metals form halides, which are salts of the relevant hydrogen halide acids:

$$Ca + Cl_2 = CaCl_2$$

Metals can combine with hydrogen to form hydrides. The reaction usually proceeds at a temperature of 350-400 °C:

$$Ca + H_2 = CaH_2$$

The reactions of metals with acids and salts are typical. If a metal reacts with an acid whose anion is not an oxidizing agent, the functions of the latter are played by the acid proton:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow$$
$$Zn^0 - 2e^- \rightarrow Zn^{2+}$$
$$2H^+ + 2e \rightarrow H_2$$

Metals forming amphoteric oxides and hydroxides also react with alkalies:

$$Zn + 2NaOH = Na_2ZnO_2 + H_2\uparrow$$

Metals react with concentrated sulphuric and nitric acids (for greater detail, see the relevant chapters).

When a neutral metal atom reacts with aqueous salt solutions, it becomes oxidized and reduces the metal ion from a salt molecule:

$$Fe + CuSO_4 = FeSO_4 + Cu$$
$$Fe^0 - 2e^- \rightarrow Fe^{2+}$$
$$Cu^{2+} + 2e^- \rightarrow Cu^0$$

The reactions proceed in accordance with the position of the metals in the electromotive series.

Active metals react with water:

$$2Na + 2H_2O = 2NaOH + H_2\uparrow$$

Preparation. Most metals occur in nature in the form of compounds, and only a few of them (the noble and seminoble ones) occur in the native form.

The natural minerals and rock containing metal compounds are called **ores.** All the methods of recovering metals from their ores are based on reduction reactions.

The reduction of anhydrous metal compounds at high temperatures is called a **pyrometallurgical process.** Either metals or carbon are used as reducing agents.

A metal can be reduced from its oxide by another, more active metal. A particular case is the aluminothermic process, or **aluminothermics:**

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

This process is generally employed to produce refractory metals such as titanium, molybdenum, chromium, and tungsten:

$$3TiO_2 + 4Al = 3Ti + 2Al_2O_3$$

The reduction of metals by carbon (carbothermics) is of the greatest importance. These processes are based on the thermal reduction of metals from their oxides by carbon or carbon monoxide:

$$PbO + C = Pb + CO\uparrow$$

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

Hydrogen can also be used to reduce metals from their oxides:

$$CuO + H_2 = Cu + H_2O$$

$$WO_3 + 3H_2 = W + 3H_2O$$

Metals can be reduced from aqueous solutions of their salts by electrolysis. The cathode reduction of metals from solutions or melts is known as electrometallurgy.

Some of the production methods will be treated in greater detail when studying the specific representatives of the metals.

Alloys. A feature of metals is their ability to mix with one another in the molten state and form homogeneous mixtures that remain homogeneous after cooling. The systems formed when a molten mixture of metals solidifies are called **alloys.** In a broader sense, alloys can be considered as macroscopically homogeneous systems consisting of two or more metals (more rarely of metals and non-metals). The structure of alloys can vary. The constituents of alloys may form either a solid solution, or a macroscop-

ically homogeneous mechanical mixture, or a chemical compound (intermetallic compounds). The type of alloy obtained depends on the activity of the metals. Systems that are solid solutions form between metals of the same group or between metals with close atomic radii.

The chemical bond in alloys is a metallic one, hence they have electrical and thermal conductance, a metallic lustre, etc.

When metals react with one another, the formed compounds differ in their properties from those of the constituents. The formulas of intermetallic compounds do not meet the classical notions on the valence of elements.

Alloys generally have a lower melting point than those of their constituent metals. The hardness of alloys is much higher than that of its components. The resistance to corrosion of many alloys is higher than that of the individual metals.

Questions and Problems

1. What is the relation between the position of a metal in the periodic table of elements and the electromotive series?

2. How are the physical properties of metals related to the metallic chemical bond?

3. Why do metals react readily with non-metals and compounds, and much more difficultly with one another?

4. Why are there much more metals than non-metals?

5[a]. A mixture of magnesium, iron, copper, and zinc powders with a mass of 2.09 g was treated with a solution of NaOH. The reaction was attended by the evolution of 0.224 lit of hydrogen. When the same amount of the mixture reacted with an acid, it displaced 0.672 lit of hydrogen, and the mass of the unreacted residue was 0.640 g. Find the composition of the mixture by mass.

6[a]. An iron plate with a mass of 100 g was immersed in a copper(II) chloride solution. After some time, the plate was extracted, dried, and weighed again. Its mass was 102 g. What mass of $FeCl_2$ formed?

7[a]. When 0.152 g of a divalent metal reacted with an acid, 140 ml of hydrogen evolved (at STP). Determine the relative atomic mass of the metal.

8[a]. To determine the content of silver in its alloy with copper, 0.5 g of the alloy was treated with nitric acid. Hydrochloric acid was added to the solution after diluting it with water. The mass of the precipitate formed was 0.430 g. Find the composition of the alloy in per cent.

9[a]. What mass of aluminium is needed to produce 1.56 g of chromium from its oxide Cr_2O_3 by aluminothermics?

10[a]. When 0.512 g of a divalent metal was roasted in the air, 0.64 g of its oxide formed. Find the relative atomic mass of the element and name it.

14.2. Corrosion of Metals

By the corrosion of metals is meant their deterioration because of the physicochemical effect of the surroundings; a metal passes into the oxidized (ionic) state and loses its inherent properties.

Corrosion in accordance with the mechanism causing it is divided into chemical and electrochemical corrosion.

Chemical corrosion implies the reaction of a metallic surface with chemically active substances (e.g. oxygen, the air) contained in natural and technological surroundings. The surface of the metal becomes oxidized without an electric current appearing in the system. The mechanism of chemical corrosion consists in the diffusion of atoms or ions of a metal through the film of products formed in corrosion and in the diffusion of atoms or ions of the oxidizing agent in the opposite direction from the surroundings.

Diffusion through an oxide film depends substantially on the presence of defects therein. At room temperature, a film often isolates the metal from the oxygen of the air, and therefore the rate of oxidation of the metal becomes negligibly small. With elevation of the temperature, the oxidation of a metal in the air occurs more intensively.

Electrochemical corrosion implies the deterioration of a metal because of its contact with electrolytes. The process is attended by the appearance of an electric current. Electrochemical corrosion can be divided into two independent processes, namely, an anode process, when a metal passes into a solution in the form of ions, and a cathode process, when the appearing electrons are attached by depolarizers. This kind of corrosion occurs when metals of various activity come into contact. Here the active metal is oxidized (donates electrons to the less active metal) and passes into a solution in the form of ions. Hydrogen ions from the solution are reduced on the less active metal, and therefore the latter does not become corroded.

Metals are protected from corrosion in various ways.

1. Protection of a metal from corrosive surroundings with the aid of a protective film. The nature of the latter may vary. Satisfactory protection from corrosion is often achieved if a metal is coated with a surface finish such as paints, lacquers, and varnishes. Sometimes a corroding metal is covered with a layer of another metal that does not corrode under the same conditions. Such coatings are called anode ones when they are made from a metal with a more negative electrode potential, and cathode ones if they are made from a metal with a more positive electrode potential.

2. Protection of metals by electrochemical means. This method is called **electroprotection,** or simply **protection.** A special anode known as a protector is used for this purpose. It is made from a metal or alloy having a more negative electrode potential than that of the metal being protected. The protector is joined to the other metal and when they are in contact they render a mutual polarizing effect. The protector will be depreciated by corrosion, but will protect the other metal. Most frequently zinc, old iron components, magnesium alloys, etc. are used as protectors. Such protection generally achieves its goal in environments that are good conductors of an electric current.

3. Protection by acting on the aggressive environment. This implies the addition of substances that greatly retard the reaction of a metal with its surroundings. These substances are called **inhibitors.**

Questions and Problems

1. Disclose the meaning of the concepts: corrosion, chemical corrosion, electrochemical corrosion, protector, inhibitor.

2. May one consider as corrosion the oxidation of aluminium in the aluminothermic process, the oxidation of iron in electric welding, and the reaction of zinc with hydrochloric acid when preparing soldering acid?

SUMMARY

Most chemical elements belong to the metals whose most important properties are the metallic type of bond in the crystal lattice, electrical and thermal conductance, a metallic lustre, ductility, and plasticity.

In the periodic table of elements, the metals are in the second to seventh periods, the number of metals growing in each following period. The most typical metals are in the bottom left part of the table, i.e. to the left of the conditional diagonal line passing from boron to astatine.

The atoms of the metals have relatively low values of the ionization energy and the largest radii for each period.

In chemical reactions, the metals exhibit exclusively reducing properties. With respect to their chemical activity, the metals form the electromotive series.

The main sources of metal production are their ores. All the methods of recovering metals are based on oxidation-reduction reactions whose essence consists in reducing a metal from its oxides.

The resistance of metals to the action of their surroundings depends on their chemical activity. The process of deterioration of a metal under the influence of the surroundings is called corrosion, which is divided into chemical and electrochemical types.

CHAPTER 15

THE ALKALI METALS

OBJECTIVES

To know the properties of the alkali metals as the most typical representatives of the metals; to be able to explain the causes of their activity and describe the most important compounds of these metals.

15.1. General

The elements of the main subgroup of Group I—lithium Li, sodium Na, potassium K, rubidium Rb, cesium Cs, and francium Fr—are known as the **alkali metals.**

The outer shell of the atoms of these elements each has one valence electron, while the preceding layers are filled up, therefore they belong to the elements of the *s* family.

Every new period begins with an alkali metal.

In comparison with other elements, the alkali metals have the lowest ionization energies and the largest atomic and ionic radii.

The increase in the atomic radius down the subgroup is attended by a decrease in the ionization energy and electron affinity, therefore the easiness of losing electrons grows. Hence, the reducing ability of the alkali metals increases down the subgroup. The number of electron shells from lithium to francium grows from two to seven. The lithium atom differs from the other alkali metals in that its layer preceding the outer one is filled by two electrons, whereas in the other atoms it is filled by eight.

Being vigorous reducing agents, they readily lose an electron and form the singly charged ion M^+.

With an increase in the nuclear charge, the metallic properties grow regularly.

The alkali metals form the hydrides MH, which are similar to NaCl in the structure of their crystal lattices. These compounds are white crystalline substances that are stable under ordinary conditions and have a high melting point. Melts of the alkali metal hydrides conduct an electric current.

The alkali metals form oxides of the M_2O type.

Occurrence and Preparation. Sodium is the most abundant of the alkali metals. The abundance of potassium is half, and of lithium one-hundredth of that of sodium. Among the sodium compounds having a great importance in industry are sodium chloride NaCl (the most abundant sodium compound), Glauber salt $Na_2SO_4 \cdot 10H_2O$, Chile nitre $NaNO_3$, cryolite Na_3AlF_6, and borax $Na_2B_4O_7$. Potassium occurs in the minerals sylvite KCl, sylvinite $KCl \cdot NaCl$, and carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$.

Lithium, sodium, and potassium are produced by the electrolytic reduction of molten salts or the relevant hydroxides. These processes can be represented, for example, by the following scheme:

$$LiCl \rightleftarrows Li^+ + Cl^-$$

$$\text{Cathode: } Li^+ + e^- = Li \qquad \text{Anode: } 2Cl^- - 2e^- = Cl_2$$

Physical Properties. All the alkali metals crystallize in a body-centred cubic lattice. In a fresh cut, they are white with a silvery metallic lustre

that rapidly vanishes in the air owing to oxidation by the oxygen of the air. This is why all the alkali metals are stored either under a layer of kerosene (paraffin), or in an atmosphere of a noble gas. They are light metals. They are very plastic and are easily cut by a knife. The hardest of the alkali metals is lithium. These metals have a high electrical and thermal conductance.

Chemical Properties. The alkali metals are strong reducing agents. When oxidized, they transform into a positive singly charged ion by the scheme

$$M - e^- \rightarrow M^+$$

This is why they have a high reactivity with respect to electronegative elements.

The alkali metals react actively with oxygen in the cold, therefore lithium, sodium, and potassium are coated with an oxide film in the air. Rubidium and cesium self-ignite in the air.

The alkali metals react vigorously with the halogens; the reaction is exothermic:

$$2Na + Cl_2 = 2NaCl \qquad 2K + Cl_2 = 2KCl$$

When heated, the alkali metals readily react with sulphur to form the sulphides M_2S:

$$2Li + S = Li_2S$$

When slightly heated, the alkali metals readily react with hydrogen. The latter gains an electron and forms the hydride ion H^- (NaH).

The alkali metals are easily oxidized by the hydrogen ion H^+ and displace H_2 from water:

$$2Na + 2HOH = 2NaOH + H_2\uparrow$$

Questions and Problems

1. Describe the relation between the atomic radii of the alkali metals and their reducing properties.

2. Describe how the outer electron level of an alkali metal atom changes when it reacts with chlorine.

3. Why are the alkali metals the most electropositive elements?

4. What is the general method of producing alkali metals? Give a specific example.

5[a]. What masses of sodium and potassium displace the same volume of hydrogen, namely, 1.12 lit, from water?

6[a]. When 2.125 g of a sodium-potassium alloy react with water, 0.84 lit of hydrogen evolved. What was the composition of the alloy in per cent?

7[a]. A specimen of metallic potassium with a mass of 1.95 g was dissolved in 50 ml of water. Find the mass of the solution and the per cent concentration by mass of the substance dissolved in it.

8[a]. Into a solution containing 16 g of NaOH, there was passed the CO_2 formed when hydrochloric acid was reacted with 23 g of potassium carbonate. What salt and how much of it formed?

9[a]. When 11.6 g of a mixture of sodium and potassium hydroxides were reacted with sulphuric acid, 28.05 g of sulphates formed. Find the composition of the mixture in per cent by mass.

10[a]. Determine the mass and composition of the formed salt when 20 g of a 10% solution of NaOH were mixed with 20 g of a 10% solution of H_2SO_4.

11[a]. A specimen of metallic sodium with a mass of 0.5 g was dissolved in water. The obtained solution was neutralized by 29.2 g of a 1.5% solution of HCl. How many grammes of sodium did the specimen contain?

15.2. Compounds

Hydroxides. Sodium and potassium hydroxides are solid white crystalline substances. They are prepared by the electrolysis of aqueous solutions of chlorides, which is used in the industry:

$$\text{Electrolyte: } 2H^+ + 2OH^- \quad 2Na^+ + 2Cl^-$$

$$\text{Cathode: } 2H^+ + 2e^- \rightarrow H_2\uparrow \quad \text{Anode: } 2Cl^- - 2e^- \rightarrow Cl_2\uparrow$$

$$\text{In solution: } 2NaOH$$

Sodium hydroxide is also prepared by the lime-soda process (causticization of soda), i.e. by treating Na_2CO_3 with calcium hydroxide:

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3\downarrow$$

This is why NaOH is called **caustic soda** in engineering.

When it is necessary to prepare especially pure hydroxides for laboratory work, the hydrolysis of the relevant alcoholate is used, for example:

$$C_2H_5ONa + HOH \rightarrow C_2H_5OH + NaOH$$

The solid hydroxides and their aqueous solutions absorb CO_2 from the atmosphere.

Potassium and sodium salts are typical ionic compounds and most of them dissolve readily in water. If a salt is formed by a weak acid, hydrolysis occurs:

$$Na_2CO_3 + HOH \rightleftarrows NaHCO_3 + NaOH$$

$$K_2S + HOH \rightleftarrows KHS + KOH$$

Potassium and sodium compounds colour a colourless flame violet and yellow, respectively, which is used for the qualitative identification of these elements.

The alkali metals are widely used in industry.

Sodium and potassium are of a tremendous biological significance. The

organism of a person with a mass of 70 kg contains 250 g of potassium and 70 g of sodium. Sodium is the main extracellular ion, and potassium is the main intracellular ion. Their ratio adjusts the osmotic pressure of the blood plasma.

Potassium is one of the elements needed for the vital activities of plants because it regulates their growth and development, water and salt metabolism, nitrogen metabolism, and respiration. The absence or decrease in the content of potassium in the soil results in the perishing of plants.

Potassium fertilizers are generally used to replenish the potassium in the soil. The important of them is sylvite KCl.

Potassium fertilizers are produced from the potassium compounds occurring abundantly in nature. In addition to sylvite, sylvinite is widely used as a fertilizer. Of major significance is the potassium sulphate formed in the processing of potassium compounds. The sodium and potassium salts widely used in engineering and medicine include their chlorides, bromides, iodides, carbonates, and hydrogen carbonates.

Questions and Problems

1. Why do all the compounds of the alkali metals have an ionic crystal lattice?

2. The alkali metal hydrides are used at laboratories as reducing agents. What is this property based on? Write the relevant equations.

3. Explain the mechanism of sodium hydride formation with an indication of the electron configurations of the formed particles.

4. What is the biological role of sodium and potassium?

5[a]. After a potassium carbonate solution was mixed with the required volume of a calcium hydroxide solution, a precipitate formed. Its mass was 40 g. How many grammes of the second product formed.

6[a]. A specimen of table salt with a mass of 10 g was treated with sulphuric acid. The evolved hydrogen chloride was dissolved in water and 50 g of a 10.95% solution were obtained. Determine the content of NaCl in the specimen in per cent by mass.

7[a]. In the electrolysis of molten sodium chloride, 56 lit of chlorine evolved at the anode. How many grammes of metallic sodium formed?

8[a]. We have a dilute solution of sodium hydroxide with a density of 1.109 g/cm^3 (at 20 °C). How many grammes of a 10% sulphuric acid solution are needed to neutralize 50 ml of this solution?

9[a]. When silicon dioxide was fused with potassium hydroxide, 77 g of a salt formed. How many grammes of KOH and SiO_2 reacted?

10[a]. A mixture of sodium carbonate and hydrogen carbonate with a mass of 30 g was heated until gases stopped evolving, after which the mass was found to be 26.9 g. How much sodium carbonate was contained in the mixture in per cent by mass?

SUMMARY

The alkali metals form the main subgroup of Group I and have the most pronounced metallic properties. This is due to the structure of the alkali metal atoms whose outer energy level has the configuration ns^1.

Every period begins with an alkali metal. They have the largest radii within a period. In the subgroup from Li to Fr, the atomic radii grow, the ionization energies diminish, and the reducing properties increase.

Being the most active metals, they react with most non-metals. The hydroxides NaOH and KOH are of the greatest importance among the sodium and potassium compounds. They are strong electrolytes.

CHAPTER 16

THE ALKALINE-EARTH METALS

OBJECTIVES

To know the features of the atomic structure of the Subgroup IIA elements; to be able to explain the laws of the change in the properties of the elements in the subgroup; to compare the properties of the elements of the given subgroup with those of the alkali metals and describe the most important compounds of calcium.

16.1. General

Subgroup IIA includes the *s* elements beryllium Be, magnesium Mg, calcium Ca, strontium Sr, barium Ba, and radium Ra. All of them are representative elements. Beryllium and magnesium differ in many respects from the other elements of the subgroup. In their properties, beryllium reminds one of aluminium, while magnesium is more similar to lithium. This is an example of the similarity between elements arranged in the periodic table in adjacent groups along a diagonal (diagonal similarity).

The elements calcium, strontium, and barium are called the alkaline-earth metals. They owe their name to the fact that their oxides (the alchemists called them "earths") when dissolved in water form alkalies.

The electron configurations of the atoms of Subgroup IIA elements are given below:

$_{4}Be—1s^2 2s^2$ (2nd period)

$_{12}Mg—1s^2 2s^2 2p^6 3s^2$ (3rd period)

$_{20}Ca—1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ (4th period)

$_{38}Sr—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ (5th period)

$_{56}Ba—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ (6th period)

$_{88}Ra—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$ (7th period)

The atomic radii increase from beryllium to radium, and the metallic activity increases in the same sequence.

The subgroup elements are oxidized by oxygen. The presence of a firm oxide layer on the surface of beryllium and magnesium protects them from further oxidation, therefore these metals can be stored in the air under ordinary conditions. The ability of the remaining metals to become oxidized grows from calcium to radium. Calcium reacts with oxygen more vigorously than magnesium, while strontium, barium, and radium react still more vigorously with it. This is why they are stored, like the alkali metals, under a layer of kerosene (paraffin). At high temperatures, all the metals except beryllium are oxidized vigorously; the other elements of the subgroup can be oxidized directly by hydrogen with the formation of hydrides:

$$M + H_2 = MH_2$$

Beryllium does not virtually react with water; magnesium reacts with it very slowly, but with elevation of the temperature, the reaction rate grows. This behaviour of beryllium and magnesium is explained by the very low solubility of their hydroxides. Calcium, strontium, and barium react with water vigorously, replacing the hydrogen.

Dilute acids react readily with the metals of this subgroup, which replace the hydrogen. Only beryllium reacts with solutions of alkalies because the hydroxide $Be(OH)_2$, having amphoteric properties, reacts with the excess alkali and forms a complex compound:

$$Be + 2H_2O + 2KOH = K_2[Be(OH)_4] + H_2\uparrow$$

Questions and Problems

1. Describe the structure of the outer electron shells of Subgroup IIA elements and explain why beryllium and magnesium are not related to the alkaline-earth metals.
2. In what respects is magnesium similar to and different from the alkaline-earth metals?
3. Indicate the common and different features of the alkaline-earth and alkali metals.
4. Why is it possible to store magnesium under ordinary conditions, and impossible to store calcium?
5[a]. When 1.97 g of a divalent metal reacted with chlorine, 3 g of its chloride formed. Determine the relative atomic mass of the metal and name it.
6[a]. A mixture of calcium and barium with a mass of 1.085 g was treated with a solution of hydrochloric acid. The volume of the evolved hydrogen was 336 ml. What was the composition of the initial mixture in per cent by mass?

16.2. Calcium

Calcium, like magnesium, is one of the most abundant elements. Its content in the Earth's crust reaches 3.5%. It is contained in rock, in sea and river water, in plants and animal organisms.

The most abundant natural compounds of calcium are chalk, marble, limestone—varieties of calcium carbonate $CaCO_3$, gypsum $CaSO_4 \cdot 2H_2O$, phosphorites $Ca_3(PO_4)_2$, and also various silicates.

Calcium is prepared by the electrolysis of a melt consisting of six parts by mass of calcium chloride and one part by mass of calcium fluoride. The presence of the latter is needed to lower the melting point of the $CaCl_2$.

Physical Properties. Calcium, like the other metals of this subgroup, is a light, hard metal. In a fresh cut, it is whitish-gray. Calcium can be turned, drawn into a wire, forged, and pressed.

Chemical Properties. Calcium is exceedingly active. Already in the air, it becomes rapidly coated with an oxide layer, while if it is ignited, it burns with a bright reddish flame:

$$2Ca + O_2 = 2CaO$$

Calcium reacts vigorously with other oxidizing agents such as the halogens, sulphur, and phosphorus. For example:

$$Ca + Cl_2 = CaCl_2; \qquad Ca + S = CaS$$

With hydrogen, calcium forms a hydride:

$$Ca + H_2 = CaH_2$$

Calcium hydride, like the other hydrides of the alkali and alkaline-earth metals, reacts actively with water to form calcium hydroxide and hydrogen:

$$CaH_2 + 2HOH = Ca(OH)_2 + 2H_2\uparrow$$

Calcium is oxidized very readily by water and acids, and it reduces hydrogen from the latter:

$$Ca + 2H_2O = Ca(OH)_2 + H_2\uparrow$$
$$Ca + 2HCl = CaCl_2 + H_2\uparrow$$

The most important compound of calcium is its oxide (quicklime), CaO. It is produced commercially by the thermal decomposition of calcium carbonate:

$$CaCO_3 = CaO + CO_2\uparrow$$

Calcium oxide is a basic one. It reacts readily with water to form calcium hydroxide (slaked lime), $Ca(OH)_2$:

$$CaO + HOH = Ca(OH)_2$$

This process is known as the **slaking of lime.**

At high temperatures, calcium oxide reacts with coke to form calcium carbide and carbon monoxide:

$$CaO + 3C = CaC_2 + CO\uparrow$$

Calcium carbide CaC_2 is widely used to produce acetylene C_2H_2.

Calcium hydroxide $Ca(OH)_2$ is a strong base. One litre of water dissolves 1.56 g of calcium hydroxide. Its saturated solution in water is called **lime water** and has an alkaline reaction. Calcium hydroxide is the most abundant and available base.

Calcium carbonate $CaCO_3$ is the most abundant calcium compound; it is insoluble in water. A solution of $Ca(OH)_2$ when standing in the air becomes turbid owing to its reaction with CO_2:

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$

Calcium carbonate is used to produce calcium oxide CaO.

The most important salts of calcium—the sulphate, phosphates, and chloride—were considered when describing the salts of the relevant acids.

Calcium is of a major significance. A human organism contains 0.7-1.4% of calcium whose main mass is concentrated in the bone tissues. The human organism needs about one gramme of calcium every day.

Calcium together with magnesium, potassium, and sodium ions are indispensable elements in the vital activities of cells.

Questions and Problems

1. Prove by indicating reaction equations that calcium is an alkaline-earth metal.
2. Why does calcium hydroxide dissolve more poorly in water than potassium hydroxide?
3. Why does lime water become turbid when left standing in the air, while potassium hydroxide does not?
4. Give reaction equations proving that calcium precedes hydrogen in the electromotive series.
5. Give reaction equations in the molecular and ionic forms proving that CaO is a basic oxide and $Ca(OH)_2$ is a base.
6[a]. What volume of CO_2 evolves when 23 g of dolomite $CaCO_3 \cdot MgCO_3$ containing 20% by mass of impurities is roasted?
7[a]. A mixture of calcium and barium oxides with a mass of 2.09 g was dissolved in water, and CO_2 was passed into the solution until the formation of a precipitate terminated. The mass of the precipitate obtained was 2.97 g. Determine the composition of the mixture in per cent by mass.
8[a]. Find the per cent concentration by mass of calcium hydroxide in a solution obtained by dissolving 0.03 g of calcium oxide in 25 ml of water.
9[a]. A limestone specimen with a mass of 2 g was roasted to a constant mass. The volume of the evolved CO_2 was 331 ml. What was the content of $CaCO_3$ in the limestone specimen in per cent by mass?

16.3. Water Hardness, Its Cause and Remedies

By water hardness is meant a property of natural water determined by the presence therein mainly of dissolved calcium and magnesium salts. **Carbonate hardness** (the presence of magnesium and calcium hydrogen carbonates) and **non-carbonate hardness** (the presence of salts of strong acids

such as calcium and magnesium chlorides or sulphates) are distinguished. The sum of the carbonate and non-carbonate hardnesses determines the total hardness.

The need to eliminate water hardness is due primarily to the undesirable effects resulting from its properties. For instance, when soap is dissolved in hard water, a precipitate of calcium and magnesium stearates forms. This explains the insignificant foaming and the inferior detergent effect of soap.

The action of heat on hard water causes the formation of scale on the walls of metal structural members (steam boilers, pipes, etc.). This requires the additional consumption of heat energy because scale is a poor heat conductor. Corrosion processes occur much more rapidly in hard water.

Carbonate hardness is also called **temporary** because when water with such hardness is boiled for a long time, the hydrogen carbonates dissolve:

$$Ca(HCO_3)_2 \xrightarrow{t} CaCO_3\downarrow + CO_2\uparrow + H_2O$$

$$Mg(HCO_3)_2 \xrightarrow{t} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

Water hardness due to the presence of magnesium and calcium chlorides or sulphates is called **permanent**. This hardness can be eliminated by chemical means, for example by the addition of sodium carbonate or calcium hydroxide:

$$CaSO_4(sol) + Na_2CO_3(sol) = CaCO_3\downarrow + Na_2SO_4(sol)$$

$$Ca(HCO_3)_2(sol) + Ca(OH)_2(sol) = 2CaCO_3\downarrow + 2H_2O$$

$$MgSO_4(sol) + Ca(OH)_2(sol) = Mg(OH)_2\downarrow + CaSO_4(sol)$$

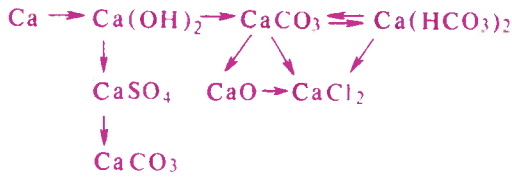
Sodium phosphates, borax, potassium carbonate, and other salts are also used to remove Ca^{2+} and Mg^{2+} ions from water.

Recent years have seen the widespread introduction of the ion-exchange method of remedying water hardness. High-molecular organic compounds known as ion exchangers are used for this purpose. They exchange the cations H^+ or anions OH^- they contain for the relevant ions in a solution. Cation and anion exchangers are distinguished. Cation exchangers (Cat. Ex.) are used to bind the Ca^{2+} cations by the reaction:

$$2[Cat.\ Ex.]H + Ca^{2+} = [Cat.\ Ex.]_2Ca + 2H^+$$

Questions and Problems

1. Why does the hardness of water have to be eliminated?
2. How can water become hard in nature? Defend your answer.
3. How can the following transformations be conducted:



4[a]. Into a solution containing 2.96 g of $Ca(OH)_2$ there were passed 1.5 lit of CO_2. What salt and how many grammes of it formed?

5[a]. An excess of a Na_2CO_3 solution was added to 10 ml of a calcium chloride solution. The precipitate formed was filtered off and roasted to a constant mass of 1.12 g. Find the per cent concentration by mass of the calcium chloride in the analyte solution.

SUMMARY

The main subgroup of Group II includes beryllium, magnesium, calcium, strontium, barium, and radium. Calcium, strontium, and barium are called the alkaline-earth metals.

Calcium is an active metal and reacts with both simple substances and water and acids.

Calcium oxide and hydroxide have pronounced basic properties. When they react with carbon dioxide, an insoluble carbonate forms.

The presence of carbonates, hydrogen carbonates, sulphates, and chlorides of magnesium and calcium in water determines its hardness. Carbonate (temporary) hardness and non-carbonate (permanent) hardness are distinguished. Hardness is eliminated by chemical or physicochemical methods.

CHAPTER 17

THE SUBGROUP IIIA. ALUMINIUM

OBJECTIVES

To know the electron configurations of the outer energy levels of the Subgroup IIIA elements; to be able to explain the laws of the changes in the structure and properties of the elements in the subgroup; to know the properties of aluminium and its compounds.

17.1. General

Boron B, aluminium Al, gallium Ga, indium In, and thallium Tl form the main subgroup of Group III. The outer energy levels of these elements contain three electrons with the configuration ns^2np^1.

The metallic properties grow within the subgroup from boron to thallium.

The electron configurations of the atoms of the Subgroup IIIA elements are given below:

$_5B—1s^2 2s^2 2p^1$ (2nd period)
$_{13}Al—1s^2 2s^2 2p^6 3s^2 3p^1$ (3rd period)
$_{31}Ga—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$ (4th period)
$_{49}In—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^1$ (5th period)
$_{81}Tl—1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^1$ (6th period)

When an atom is excited, one of the *s* electrons of the outer energy level passes into a free orbital of the *p* sublevel. This state corresponds to a valence of three:



Ground state Excited state

Compounds in which the elements exhibit an oxidation state of +3 are the most stable.

The elements of Subgroup IIIA form the oxides R_2O_3, namely, the acid one B_2O_3, the amphoteric ones Al_2O_3, Ga_2O_3, and In_2O_3, and the basic oxide Tl_2O_3. The oxides B_2O_3, Al_2O_3, and Ga_2O_3 dissolve readily in alkalies, In_2O_3 dissolves sparingly in them, while Tl_2O_3 does not dissolve at all. The weak acid H_3BO_3 corresponds to the oxide B_2O_3; the hydroxides $Al(OH)_3$, $Ga(OH)_3$, and $In(OH)_3$ are amphoteric.

Questions and Problems

1. Which of the elements Be, B, Mg, Al, and Ga has the greatest (a) metallic, and (b) non-metallic properties. Defend your answer.
2. How and why do the properties of the oxides and hydroxides of the Subgroup IIIA elements change?

17.2. Aluminium

Aluminium is the most abundant metal in nature (its total content in the Earth's crust is about 9%). It is contained in silicates (spars, mica), and also in the clays formed from feldspars in their natural deterioration. The most important aluminium compounds are Al_2O_3 (corundum, ruby, sapphire), orthoclase $KAlSi_3O_{10}$, albite $NaAlSi_3O_{10}$, anorthite $Ca(AlSiO_4)_2$, nepheline $KNaAlSiO_4$, cryolite Na_3AlF_6, and bauxite $Al_2O_3 \cdot H_2O$.

Preparation. The modern industrial method of producing aluminium consists in the electrolysis of aluminium oxide, which has a high melting point (2045 °C) and does not conduct an electric current. This is why Al_2O_3 is dissolved in molten cryolite Na_3AlF_6 with the simultaneous addition of fluorides (CaF_2, MgF_2, or AlF_3). This mixture melts at about 1000 °C.

In electrolysis, aluminium is deposited on the cathode, while oxygen evolves at the anode:

$$Al_2O_3 \xrightarrow{\text{electrolysis}} 2Al + 1.5O_2$$

The evolved oxygen reacts with the carbon anode to form CO and CO_2. Since the carbon electrode is gradually used up, it is periodically renewed. The molten aluminium gathers at the bottom of the electrolyzer, whence it is periodically tapped.

Physical Properties. Aluminium is a silvery white metal having a face-centred lattice. Its density is 2.7 g/cm^3. It is a light metal and is a good conductor of electricity and heat.

Chemical Properties. The most typical oxidation state of aluminium is +3. Having a great affinity to oxygen, aluminium oxidizes very readily and forms the oxide Al_2O_3:

$$4Al + 3O_2 = 2Al_2O_3$$

Such oxidation in the air causes a strong protective film of the oxide to form closely adhering to the surface of the metal. This is exactly what explains the high stability of aluminium articles under atmospheric conditions, in sea water, etc. The oxide film protects the metal from further oxidation.

If the oxide film is removed from the surface of the metal, the latter reacts vigorously with water, displacing hydrogen:

$$2Al + 6HOH = 2Al(OH)_3 + 3H_2\uparrow$$

Aluminium becomes passivated in concentrated nitric and sulphuric acids in the cold owing to the formation of a protective film. It reacts readily with other mineral acids, displacing hydrogen:

$$2Al + 6HCl = 2AlCl_3 + 3H_2\uparrow$$

Being amphoteric, aluminium readily reacts with alkali solutions:

$$2Al + 6NaOH + 6H_2O = 2Na_3[Al(OH)_6] + 3H_2$$

Aluminium reacts with dilute sulphuric acid when slightly heated, displacing hydrogen:

$$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2\uparrow$$

Dilute nitric acid reacts with aluminium and is reduced to nitrogen monoxide:

$$Al + 4HNO_3 = Al(NO_3)_3 + NO\uparrow + 2H_2O$$

At room temperature, aluminium reacts with the halogens to form salts of the relevant hydrohalic acids:

$$2Al + 3Cl_2 = 2AlCl_3$$

Aluminium reduces many metals from their oxides. This property of aluminium is widely used in the production of metals (aluminothermics):

$$3Fe_3O_4 + 8Al = 4Al_2O_3 + 9Fe$$

Aluminium oxide Al_2O_3 is a white refractory substance. It is encountered in nature as the mineral corundum.

Aluminium oxide is insoluble in water. It has an amphoteric nature, its basic properties being more pronounced than its acidic ones:

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O$$

Hydroxoaluminates are formed with alkali solutions:

$$Al_2O_3 + 6NaOH + 3H_2O = 2Na_3[Al(OH)_6]$$

while metaaluminates are formed when aluminium oxide is fused with dry alkalies:

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$$

Aluminium hydroxide $Al(OH)_3$ is a polymeric compound having a laminar crystalline lattice. It can exist in two modifications — in the crystalline or amorphous form. In the latter case it is a white gelatinous precipitate obtained when the hydroxide is precipitated from solutions of aluminium salts.

Aluminium hydroxide is prepared by reacting an alkali with a solution of an aluminium salt:

$$AlCl_3 + 3NaOH = Al(OH)_3\downarrow + 3NaCl$$

Aluminium hydroxide is virtually insoluble in water and is a typical amphoteric hydroxide. When reacting with acids, it forms salts in which the aluminium is a cation component. When reacting with alkalies, aluminates are formed. They are complex compounds in which the aluminium is an anion component:

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$
$$Al(OH)_3 + NaOH = Na[Al(OH)_4]$$

or in the ionic form:

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$$
$$Al(OH)_3 + OH^- = [Al(OH)_4]^-$$

Aluminium salts crystallize from acidic solutions in the form of crystal hydrates such as $AlCl_3 \cdot 6H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$.

Aluminium compounds are greatly hydrolyzed in aqueous solutions:

$$AlCl_3 + HOH \rightleftarrows Al(OH)Cl_2 + HCl$$
$$Al(OH)Cl_2 + HOH \rightleftarrows Al(OH)_2Cl + HCl$$

The hydrolysis is generally incomplete and reversible, while the solution has an acid reaction.

Application. The most important sphere of application of aluminium is the production of light alloys on its basis. It is also widely used as an alloying addition to alloys based on copper, magnesium, titanium, nickel, zinc, and iron. The pure metal is used to fabricate chemical apparatus and electrical wires. Aluminium foil is used to make capacitors.

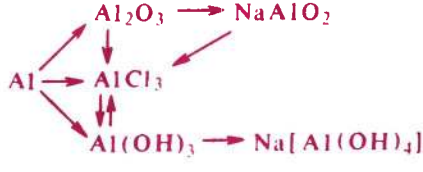
Aluminium chloride $AlCl_3$ is generally prepared by the direct reaction of chlorine with aluminium. It has found application as a catalyst in organic synthesis.

Aluminium sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ is employed in the mordant dyeing of cotton fabrics.

Alum $KAl(SO_4)_2 \cdot 12H_2O$ is used as a tanning agent in the leather and footwear industry. In medicine, it is used for cauterization and as a haemostatic agent.

Questions and Problems

1. How can manganese be produced from MnO_2 by the aluminothermic process?
2. Powders of aluminium and iodine were mixed on an asbestos screen. No reaction began until a drop of water was added to the mixture. After this, the mixture ignited, abundantly evolving puffs of a violet smoke and sheaves of sparks. When the reaction terminated, there was a white salt on the screen. Explain these phenomena and defend your answer using the theory of oxidation-reduction, the concept of the rate of chemical reactions, and your knowledge of the properties of iodine and aluminium. Give the equations of the reactions.
3. How can one prove that aluminium hydroxide is amphoteric? Substantiate your answer.
4. How can the following transformations be performed:



Write the reaction equations in the molecular and ionic forms, and indicate the reaction conditions.

5. Describe the processes occurring in an aqueous solution of aluminium chloride. What is the reaction of this solution?

6. To the atom of which noble gas and to the ion of which halogen is the particle formed when an aluminium atom loses its valence electrons similar in its electron structure?

7. Describe the industrial process of producing aluminium.

8. Aluminium hydroxide is a weak electrolyte. Explain the reason for this property and confirm it with the relevant reaction equations.

9[a]. An aluminium powder specimen with a mass of 1.240 g was treated with a 30% solution of NaOH. The volume of the evolved hydrogen was 1.344 lit. What was the content of aluminium in the specimen in per cent by mass?

10[a]. A mixture of aluminium, zinc, and magnesium powders with a mass of 1.280 g was treated with a hydrochloric acid solution. The volume of the evolved hydrogen was 0.896 lit. When the same mass of the mixture was treated with an NaOH solution, 0.560 lit of hydrogen evolved. Determine the composition of the mixture in per cent by mass.

11[a]. How many grammes of chromium can be reduced from its oxide if 9.0 g of an aluminium powder containing 25% of impurities entered into the aluminothermic reaction?

12[a]. To reduce manganese from MnO_2 by aluminothermics, 10.8 of aluminium were mixed with 26.2 g of MnO_2. Which of the reactants and how many grammes of it remained after the reaction?

13[a]. Depending on the sequence of mixing solutions of sodium hydroxide and aluminium chloride, two phenomena can be observed: if several drops of the salt solution are added to the alkali solution, no precipitate forms; if the reaction is conducted in the reverse sequence, a precipitate forms. Explain the two processes and calculate how many grammes of a 20% NaOH solution are needed for the complete precipitation of the aluminium from a solution containing 2.67 g of $AlCl_3$.

14[a]. A copper-aluminium alloy was treated with a 40% NaOH solution. The evolved gas occupied a volume of 0.846 lit. The residue was dissolved in nitric acid, then the solution was evaporated and roasted up to a constant mass, which was 0.398 g. What was the composition of the alloy?

15[a]. In the electromotive series, aluminium is far to the left of hydrogen, but does not displace it from water. When aluminium is reacted with dilute sulphuric acid, hydrogen is displaced from the latter. Explain the role of the acid and write the equations of the relevant reactions. Calculate the volume of a 20% sulphuric acid solution with a density of 1.139 g/cm^3 needed to obtain 5.6 lit of hydrogen.

16[a]. What volume of hydrogen evolves when an acid is reacted with 1 g of an alloy containing 5% of aluminium, 2% of zinc, and 93% of magnesium?

17[a]. When aluminium was heated in a chlorine atmosphere, 13.35 g of its chloride were obtained. Calculate the masses of manganese dioxide and 36% HCl needed to produce the chlorine required for the reaction.

SUMMARY

Subgroup IIIA includes boron, aluminium, gallium, indium, and thallium. The outer energy level of the atoms of these elements has the configuration ns^2np^1, hence their valence in the excited state is three.

Aluminium exhibits an oxidation state of +3 in its compounds. It reacts with oxygen to form an amphoteric oxide.

Aluminium reacts with water only after the oxide film has been removed from its surface. It reacts very vigorously with acids.

Aluminium hydroxide, like the oxide, has amphoteric properties.

CHAPTER 18

THE SUBGROUP VIIIB. IRON

OBJECTIVES

To know the structural features of the secondary subgroup of Group VIII; to be able to explain the structure of the iron atom; to know the most important properties of iron and its compounds.

18.1. General

Subgroup VIIIB includes nine *d* elements: iron Fe, ruthenium Ru, osmium Os, cobalt Co, rhodium Rh, iridium Ir, nickel Ni, palladium Pd, and platinum Pt.

In the *d* elements of Group VIII, as the *d* orbitals of the level preceding the outer one become filled, the horizontal similarity with the neighbouring *d* elements in the period grows. For example, nickel is similar in many ways not only to cobalt and iron, but also to copper. The element pairs Ru-Os, Rh-Ir, and Pd-Pt are especially close in their properties, which is why they are combined into the **platinum metal family**. Iron, cobalt, and nickel form the **iron triad** or the **iron family**.

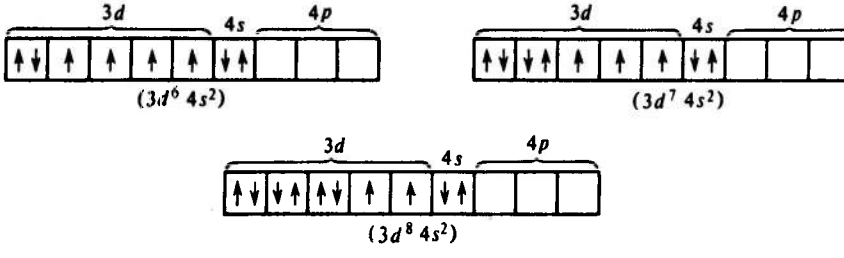
All the *d* elements of Group VIII have incomplete *d* sublevels in the levels preceding the outer one.

The electron configurations of the atoms of the iron family elements are as follows:

$_{26}$Fe—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
$_{27}$Co—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
$_{28}$Ni—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

They all belong to the fourth period.

The *s* orbital of the outer level of iron, cobalt, and nickel is populated by two electrons (an ns^2 configuration). The *d* sublevels of the levels preceding the outer one are populated by six to eight electrons, respectively:



In addition to the outer s^2 electrons, the electrons of the *d* sublevel of the preceding level participate in the formation of chemical bonds. But none of the iron triad elements reaches an oxidation state of +8 corresponding to the group number in their compounds. The oxidation states +2 and +3 are the most stable for them, the state +2 being the most typical for nickel and cobalt.

The elements of the iron triad form oxides of the type EO and E_2O_3, which the hydroxides $E(OH)_2$ and $E(OH)_3$ correspond to.

The chemical activity lowers in the series Fe-Co-Ni. In the electromotive series, these elements are to the left of hydrogen, but in their chemical activity cobalt and nickel are inferior to iron. Under ordinary conditions, they are quite stable with respect to oxygen; cobalt reacts with it at 300 °C, and nickel at 500 °C. When heated, they react with almost all non-metals—halogens, sulphur, selenium, phosphorus, arsenic, etc. and form compounds from salt-like ones ($CoHal_2$, $NiHal_2$) to metallic ones.

Cobalt and nickel react with dilute acids, displacing hydrogen and becoming oxidized to Co(II) and Ni(II). They react considerably more slowly with acids than iron. Concentrated HNO_3 passivates all three metals.

Questions and Problems

1. How does the unfilled structure of the *d* sublevel of the outer level affect the properties of the Subgroup VIIIB elements?
2. Why is the oxidation state +2 a stable one for the iron family elements?
3. Iron and calcium each has two *s* electrons in their outer energy level. What explains the sharp difference in their chemical activity?

18.2. Iron

After aluminium, iron is the most abundant element. Its content in the Earth's crust reaches 5%. Iron occurs on the Earth's surface mainly in the form of compounds in deposits of iron ores. The following iron compounds are the most important: magnetite Fe_3O_4, red iron ore or haematite Fe_2O_3, brown iron ore or limonite $Fe_2O_3 \cdot nH_2O$, spathic iron or siderite $FeCO_3$, and pyrite FeS_2.

Physical Properties. Chemically pure iron is a lustrous, silvery white plastic metal. It is considerably softer than gold and silver. It readily lends itself to forging, rolling, and other kinds of processing both in the hot and cold states. Its melting point is 1539 °C. It has magnetic properties.

Chemical Properties. Iron forms no compounds in which its oxidation state would correspond to the group number, i.e. eight. The highest oxidation state of iron is +6, but it is encountered in this state extremely rarely, for instance, in K_2FeO_4. The +2 and +3 oxidation states correspond to the Fe^{2+} and Fe^{3+} ions, which have six and five electrons, respectively,

in the unfilled 3*d* orbital. The magnetic properties of iron compounds are due to the presence of a smaller number of electrons in the 3*d* sublevel than is needed for filling it.

Iron belongs to metals with a moderate reducing activity. It follows zinc in the electromotive series. At an ordinary temperature, it is oxidized very slowly by the oxygen of the air, but heated iron readily burns with the formation of iron(III) oxide:

$$4Fe + 3O_2 = 2Fe_2O_3$$

In the presence of moisture, iron oxidizes in the air more rapidly, and it rusts, i.e. becomes covered with a layer of hydrated iron(III) oxide:

$$4Fe + 3O_2 + nH_2O = 2Fe_2O_3 \cdot nH_2O$$

In the presence of traces of moisture, iron is readily oxidized by chlorine to form iron(III) chloride:

$$2Fe + 3Cl_2 = 2FeCl_3$$

Oxidation by weak oxidizing agents leads to the formation of Fe^{2+}, while strong oxidizing agents transfer it into Fe^{3+}.

When heated, iron reacts with many non-metals:

$$Fe + S = FeS$$

Heated iron reacts with water with the formation of Fe_3O_4 and the evolution of hydrogen:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2\uparrow$$

Iron reacts with dilute hydrochloric and sulphuric acids and displaces hydrogen from them:

$$Fe + 2HCl = FeCl_2 + H_2\uparrow$$
$$Fe + H_2SO_4 = FeSO_4 + H_2\uparrow$$

Concentrated nitric and sulphuric acids passivate iron. When heated, these acids oxidize iron to Fe^{3+}:

$$2Fe + 6H_2SO_4 = Fe_2(SO_4)_3 + 3SO_2\uparrow + 6H_2O$$
$$Fe + 4HNO_3 = Fe(NO_3)_3 + NO\uparrow + 2H_2O$$

In aqueous solutions, iron reduces metals to the right of it in the electromotive series:

$$Fe + CuSO_4 = FeSO_4 + Cu$$

Questions and Problems

1. Why does iron become oxidized to Fe^{2+} with dilute sulphuric acid, while it either does not react at all with concentrated acid or when heated becomes oxidized to Fe^{3+}?

2. Explain the balancing of the equations of the oxidation-reduction reactions contained in this section by the electron balance and ion-electron methods.

3. How can the oxidation of iron be prevented?

4[a]. What mass of iron(II) sulphate can be obtained when dissolving the calculated (stoichiometric) mass of iron in 30 ml of 30% sulphuric acid with a density of 1.219 g/cm^3?

5[a]. By how many grammes will the mass of an iron plate immersed in a $CuSO_4$ solution grow if 20.8 g of metallic copper were deposited on the plate?

6[a]. A specimen of an iron powder with a mass of 0.32 g displaced 0.112 lit of hydrogen when treated with an acid. What was the content of the iron in the specimen in per cent by mass?

7[a]. In 50 g of 20% sulphuric acid there were dissolved 3.36 g of iron. What is the per cent concentration by mass of the $FeSO_4$ in the solution? How many grammes of acid remained in the solution?

18.3. Iron Compounds

Iron forms the oxides FeO and Fe_2O_3. **Iron(II) oxide** can be prepared by the incomplete reduction of magnetite Fe_3O_4 by carbon monoxide:

$$Fe_3O_4 + CO = 3FeO + CO_2\uparrow$$

FeO is a black crystalline substance insoluble in water and alkalies. It reacts with acids to form the relevant salts:

$$FeO + 2HCl = FeCl_2 + H_2O$$

The hydroxide $Fe(OH)_2$ obtained from iron(II) salts by their reaction with alkalies corresponds to the oxide FeO. This hydroxide has a pronounced basic nature. It readily enters into reactions with acids:

$$Fe(OH)_2 + 2HCl = FeCl_2 + 2H_2O$$
$$Fe(OH)_2 + CH_3COOH = Fe(CH_3COO)_2 + 2H_2O$$

In the presence of the oxygen of the air, $Fe(OH)_2$ rapidly oxidizes to $Fe(OH)_3$, therefore the white precipitate of $Fe(OH)_2$ rapidly darkens:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$$

Iron(III) oxide Fe_2O_3 is a red-brown powder insoluble in water. It is obtained when roasting pyrite.

Fe_2O_3 exhibits weak amphoteric properties. It reacts with acids to form iron(III) salts, and with alkalies to form salts where the iron is in the acid residue:

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$
$$Fe_2O_3 + 2NaOH \xrightarrow{\text{fusion}} \underset{\text{Ferrite}}{2NaFeO_2} + H_2O$$

Iron(III) hydroxide $Fe(OH)_3$ is a red-brown precipitate varying in its composition: $Fe_2O_3 \cdot nH_2O$. It gradually loses water and transforms into Fe_2O_3. Iron(III) hydroxide is a weaker base than $Fe(OH)_2$ and exhibits amphoteric properties (with basic ones predominating). In the presence of di-

lute mineral acids, $Fe(OH)_3$ readily forms the relevant salts. When $Fe(OH)_3$ reacts with concentrated alkalies, stable complexes form:

$$Fe(OH)_3 + 3KOH = K_3[Fe(OH)_6]$$

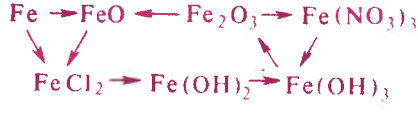
Iron plays an exclusively important biological role because it is contained in haemoglobin and some enzymes. Haemoglobin combines with oxygen and carries it from the lungs to the muscles, where it is transferred to myoglobin, after which the haemoglobin picks up CO_2 and carries it to the lungs. A lack of iron in an organism results in diseases such as anaemia.

Questions and Problems

1. Propose methods of performing the transformations:

$$Fe^0 \rightarrow Fe^{2+} \qquad Fe^0 \rightarrow Fe^{3+}$$
$$Fe^{2+} \rightarrow Fe^{3+} \qquad Fe^{3+} \rightarrow Fe^{2+}$$
$$Fe^{3+} \rightarrow Fe^0 \qquad Fe^{2+} \rightarrow Fe^0$$

2. How can the following transformations be performed:



3. Explain the hydrolysis of the salt $FeCl_3$.

4[a]. What volume of oxygen is required to oxidize 18 g of $Fe(OH)_2$ to $Fe(OH)_3$?

5[a]. When an ammonia water solution was added to 50 g of an iron(III) chloride solution, iron(III) hydroxide formed whose decomposition yielded 1.60 g of Fe_2O_3. What was the per cent concentration by mass of the $FeCl_3$ in the solution?

6[a]. Iron(II) sulphate, being a reducing agent, reacts with $KMnO_4$ in an acid medium as follows:

$$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow$$
$$\rightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$$

Balance the equation and calculate the mass of a 0.5% solution of $KMnO_4$ needed to oxidize 7.6 g of $FeSO_4$.

7[a]. The heating of 5.56 g of iron(II) sulphate crystal hydrate yielded 3.04 g of the anhydrous salt. Determine the formula of the crystal hydrate.

18.4. Production of Iron and Its Alloys

To extract iron from its ores, the oxides contained in the latter are reduced in the presence of coke and limestone. The entire process is conducted in a blast furnace, which is shown schematically in Fig. 31.

When the coke burns, carbon dioxide forms:

$$C + O_2 = CO_2\uparrow$$

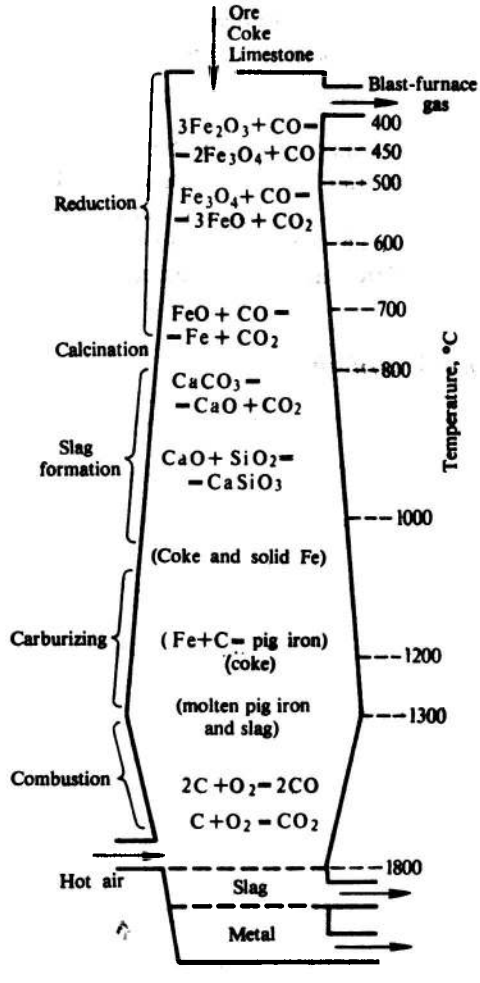


Fig. 31
The blast furnace process

The CO_2 passes through the red-hot coke and transforms into CO:

$$CO_2 + C = 2CO\uparrow$$

At a temperature of 450-500 °C, the carbon monoxide reduces the iron(III) oxide to Fe_3O_4:

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2\uparrow$$

At a higher temperature (600 °C), the Fe_3O_4 is reduced to iron(II) oxide:

$$Fe_3O_4 + CO = 3FeO + CO_2\uparrow$$

Further, at a temperature of 700 °C, the iron(II) oxide is reduced to metallic iron:

$$FeO + CO = Fe + CO_2\uparrow$$

Since iron ores contain compounds of silicon, manganese, and phosphorus as impurities, reducing processes also occur with them:

$$SiO_2 + 2CO \rightarrow 2CO_2 + Si$$
$$MnO_2 + 2CO \rightarrow 2CO_2 + Mn$$

The barren rock in the ore consists mainly of silicon dioxide. To transfer such refractory impurities into more low-melting compounds, fluxes such as calcium carbonate are added to the ore. The siliceous impurities contained in the ore react with the calcium oxide formed when the $CaCO_3$ decomposes. The calcium silicate $CaSiO_3$ is easily separated in the form of slag.

The product of the blast furnace process, after being tapped from the furnace and cooled in moulds, is called **pig iron**. It contains 3-4% of carbon, and also admixtures of silicon, sulphur, phosphorus, and manganese. Pig iron is brittle and does not lend itself to forging or rolling. Several grades of pig iron are distinguished including white pig iron, gray pig iron, and special pig iron.

In gray pig iron, the carbon is present in the form of free graphite; this iron is used for casting, and the products are now said to be made of **cast iron**. White pig iron contains iron carbide Fe_3C called **cementite**. This iron is very hard and brittle and is generally used to produce steel. The addition of phosphorus to pig iron makes it more malleable. This property is widely used to produce art castings.

Steel is an alloy of iron and carbon and contains the very insignificant impurities present in cast iron. The carbon content in steel ranges from 0.1 to 1.5%. The strength of steels grows with an increase in their carbon content. Steels are produced from pig iron. Three methods are mainly used in metallurgy to process pig iron into steel, namely, the Bessemer process, the open-hearth process, and the smelting of steel in electric furnaces.

To convert pig iron into steel, most of the impurities have to be removed from it. A way of removing them was proposed by Henry Bessemer (the Bessemer process). It is used to process pig iron with an increased content of silicon, manganese, and carbon. These elements are oxidized in a special apparatus called a converter:

$$Si + O_2 = SiO_2$$
$$Mn + O_2 = MnO_2$$
$$C + O_2 = CO_2\uparrow$$

and insignificantly:

$$2Fe + O_2 = 2FeO$$

All these reactions are exothermic. A stream of air enriched in oxygen is blown through the molten iron, where the oxidation process occurs. The resulting oxides SiO_2, MnO_2, and CO_2 are removed in the form of gases (CO_2) or a slag:

$$SiO_2 + MnO \rightarrow MnSiO_3$$
$$SiO_2 + MgO \rightarrow MgSiO_3$$
$$SiO_2 + FeO \rightarrow FeSiO_3$$

The Bessemer process is also known as the converter one. The steel obtained in this way is of a higher quality than that produced in an open-hearth furnace.

The **open-hearth process** unlike the converter one can be used to process irons varying in composition. The iron is melted in a flame reverberatory furnace.

Steels are classified according to their designation as tool and instrument, structural, and special ones, and according to their chemical composition as carbon and special steels.

Questions and Problems

1. What is the difference between the blast-furnace and Bessemer processes?
2. Can natural gas CH_4 be used in a blast furnace instead of coke?
3[a]. When a specimen of steel with a mass of 8 g was burned in oxygen, 0.1 g of CO_2 was obtained. What was the carbon content in the steel in per cent by mass?
4[a]. What mass of pig iron containing 94% of iron can be produced from one tonne of red iron ore containing 20% of impurities?
5[a]. What volume of CO is needed to prepare 11.2 g of iron from Fe_2O_3?
6[a]. A specimen of ore with a mass of 10 g containing Fe_2O_3 was reduced and 5.6 g of iron were obtained. What is the content of Fe_2O_3 in the ore in per cent by mass?
7. Iron may occur in nature in the form of the carbonate $FeCO_3$ that can also be used as iron ore. Compile the equations of the reactions that can occur with this substance in a blast furnace.

SUMMARY

Iron is an element of a triad also including cobalt and nickel. This triad together with the platinum metals belongs to Subgroup VIIIB.

Iron is produced in the industry in various ways.

Being an active metal, iron reacts with many simple substances, and also with water and acids.

Iron forms two types of oxides—FeO and Fe_2O_3. Iron(II) oxide has basic properties, while iron(III) oxide has amphoteric properties, but with the obvious predomination of basic ones.

Part III
ORGANIC CHEMISTRY

CHAPTER 19
FUNDAMENTALS

OBJECTIVES

To formulate the concepts "organic chemistry" and "organic substance"; to set out the fundamentals of the theory of organic compound structure; to substantiate and explain the classification of organic compounds; to explain the concepts of a functional group, homologous series, and isomerism, and also to know the classification of organic reactions; to indicate the mechanism of a displacement reaction proceeding from the nature of the displacing particle; to use the rules of the IUPAC system of nomenclature for forming the names of organic compounds; to compile the structural formula of a compound proceeding from the proposed nomenclature system; to form the name of a compound in accordance with its structural formula; to give examples of structural isomerism; to correctly depict the structural formulas of geometrical isomers.

19.1. The Subject of Organic Chemistry

By gradually accumulating knowledge in the field of chemical and biochemical transformations of organic substances, people learned how to conduct various experiments with organic substances. First this was generally a transformation of complex substances into simpler ones, for example, the fermentation of sugar yielded ethanol and vinegar, and the oxidation of fossil resin—amber—yielded succinic acid.

The oxidation of sugar yields formic acid, which before such reactions were conducted was known to be a substance of an animal origin. It was later found that fats, carbohydrates and other substances are typical of both plants and animal organisms.

Results obtained by outstanding chemists including F. Wöhler (the synthesis of oxalic acid and urea), H. Kolbe (the synthesis of acetic acid), M. Berthelot (the synthesis of fats and the preparation of acetylene from carbon and hydrogen), and A. Butlerov (the synthesis of a saccharide substance from formaldehyde) showed the close relation between organic and

inorganic substances, and also the possibility of the mutual transformation of substances.

A qualitative feature of organic chemistry is the fact that it studies not carbon itself, but the hydrocarbons and their derivatives. This is why *organic chemistry is the chemistry of hydrocarbons and their derivatives,* which more accurately reflects the content of this subject.

The number of carbon compounds is much greater than all the other ones not containing carbon. This diversity is due to the structure of the carbon atom, which is capable of: (1) forming stable bonds not only with other atoms, but also with other carbon atoms, the result being the formation of chains and rings; (2) forming single, double, and triple bonds not only with like atoms, but also with other elements because of the different type of hybridization; and (3) combining with other carbon atoms, which allows carbon chains to branch out and produce a multitude of complicated structures.

The place occupied by organic chemistry among the sciences is due to many factors, the most important of which are the large number and diversity of organic compounds, the presence of specific properties distinguishing organic substances from compounds of other elements, and their exceedingly great significance in the life of humans.

Questions and Problems

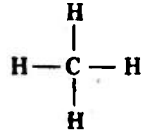
1. Why has the given branch of chemistry been named "organic chemistry"?
2. Organic chemistry is sometimes called the chemistry of carbon compounds. Is this name completely correct? Why?
3. What is the reason for the existence of a multitude of organic substances?
4. Why has organic chemistry been singled out into a separate science?

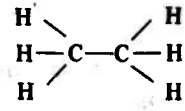
19.2. The Structural Theory

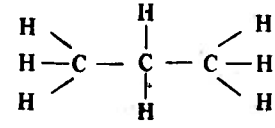
The development of organic chemistry in the first half of the 19th century provided the prerequisites for systematization of the accumulated scientific data on organic substances and the creating of the theoretical foundation of this science. The most important achievements included the proof of the tetravalent nature of carbon and of its ability to form chains. These and other facts were used by A. Butlerov when creating the **structural theory of organic compounds,** which is the foundation of organic chemistry. The most important tenets of the theory are as follows.

1. *A molecule of any substance is not a chaotic accumulation of atoms. All the atoms in a molecule are bonded to one another in a strictly definite sequence, and their bonding requires a definite fraction of chemical affinity.* The way atoms are bonded in a molecule was called chemical structure by Butlerov.

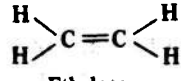
For instance, by designating each bond in methane by a dash, we can depict its structural formula, and also those of ethane C_2H_6 and propane C_3H_8:


Methane


Ethane

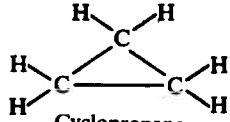

Propane

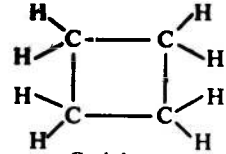
However, not only single bonds, but also double and triple ones can form between carbon atoms:

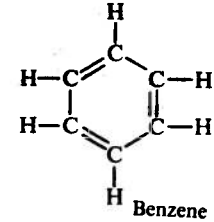

Ethylene


Acetylene

Carbon atoms can form closed chains (rings) in addition to open ones:


Cyclopropane

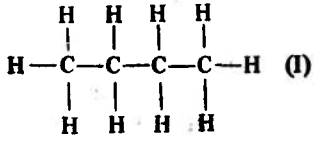

Cyclobutane


Benzene

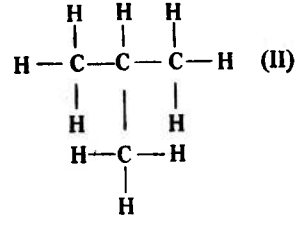
2. *The properties of substances depend on the structure of their molecules, i.e. on the way the atoms are bonded to one another.*

This tenet of the theory is the key to explaining the phenomenon of isomerism. Two or more substances having the same qualitative and quantitative composition (and relative molecular mass), but differing in the order of bonding of the atoms in the molecule, i.e. in their structure and, therefore, in their physical and chemical properties, are called **isomers**.

For example, two substances, butane and isobutane, correspond to the formula C_4H_{10}. Their structure can be represented as follows:


(I)

Butane


(II)

Isobutane

In the first case, the carbon atoms form an unbranched chain (I), and in the second, a branched chain (II). Substances I and II differ in their structure (i.e. have a different sequence of bonding of their atoms), and therefore they will also differ in their properties, i.e. will be **isomers** (butane, isobutane). The phenomenon of **isomerism** is one of the reasons for the great diversity of organic substances.

3. *By studying the products of the chemical transformation of a substance, we can determine its structure and express it by a specific structural formula.*

When setting out the following sections of organic chemistry, this tenet of the theory will be illustrated by specific examples.

4. *Both bonded atoms and atoms not directly bonded to one another mutually affect one another in molecules.*

This statement shows that the reactivity of atoms (or groups of atoms) in a molecule varies depending on which atoms they are bonded to in the given molecule. This change is due first of all to the mutual influence of atoms directly bonded to each other.

By comparing the chloroacetic acids with one another, for example, we can see that the dissociation constant grows down the series from acetic to trichloroacetic acid, the acidic properties of the latter being comparable with those of strong mineral acids:

Acid	K_{diss}
Acetic $CH_3—\overset{\overset{O}{\|}}{C}—OH$	1.75×10^{-5}
Monochloroacetic $ClCH_2—\overset{\overset{O}{\|}}{C}—OH$	1.5×10^{-3}
Dichloroacetic $Cl_2CH—\overset{\overset{O}{\|}}{C}—OH$	5×10^{-2}
Trichloroacetic $Cl_3C—\overset{\overset{O}{\|}}{C}—OH$	2×10^{-1}

The growth of the dissociation constant when the chlorine is introduced into the acid radical is explained by the fact that the chlorine, being a more electronegative element, pulls electrons away from the adjacent carbon atom, as a result of which the latter acquires a positive charge. This carbon atom, in turn, pulls electrons away from the adjacent carbon atom. Hence,

the electrons shift toward the chlorine along the entire chain of atoms, and in the long run the hydrogen atom in the carboxyl group of a chloroacetic acid is detached more readily in the form of an ion than the hydrogen in the carboxyl group of acetic acid. This electron shifting grows with an increase in the number of chlorine atoms. This is why trichloroacetic acid is the strongest one in the series.

The postulate of the mutual influence of atoms was later brilliantly confirmed and developed by the eminent organic chemist V. Markovnikov, a pupil of Butlerov.

The creation of the structural theory played a very important role in the development of organic chemistry. It transformed from a chiefly analytical science to one of synthesis. The theory of the structure of molecules set up prerequisites for explaining and predicting different kinds of isomerism of organic molecules, and also the directions and mechanisms of chemical reactions.

Questions and Problems

1. Disclose the essence of the concept "isomerism".
2. Why is the existence of isomers possible?
3. How is the mutual influence of atoms in a molecule expressed?

19.3. Classification

The structure and properties of organic substances, notwithstanding their large number and diversity, can be studied owing to a harmonious system of classifying them. Proceeding primarily from the structural theory, it takes into account the following most important features:

(1) the structure of the backbone or skeleton of a molecule;

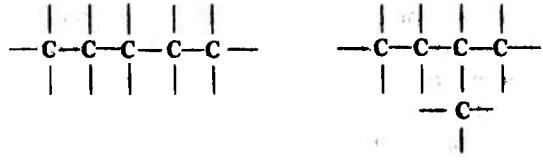
(2) the degree of saturation determined by the nature of the bond between the carbon atoms;

(3) the presence of functional groups and their nature.

Not only carbon atoms, but also other ones called **heteroatoms** (e.g. O, S, N, and P) can participate in forming the skeleton of a molecule. They can combine with one another in a diverse sequence, forming **branched** and **unbranched (linear)** chains, **open** and **closed** chains (the latter are also called **rings**).

Accordingly, all organic compounds are divided into three main groups or series.

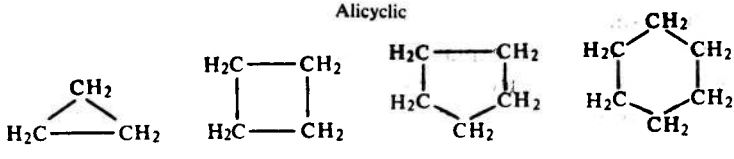
1. Aliphatic (Acyclic) Compounds. These include compounds whose molecules contain open (branched or unbranched) chains:



Unbranched chain Branched chain

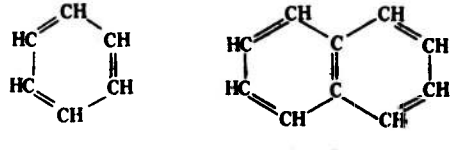
2. Carbocyclic Compounds. The molecules of compounds belonging to this group or series contain rings formed only by carbon atoms. Alicyclic and aromatic compounds are distinguished within this group. Some examples are:

Alicyclic



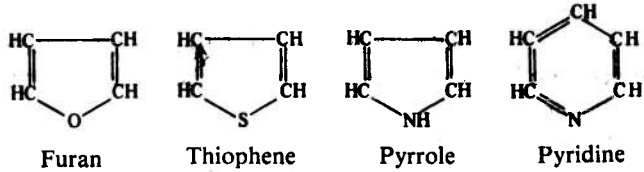
Cyclopropane Cyclobutane Cyclopentane Cyclohexane

Aromatic



Benzene Naphthalene

3. Heterocyclic Compounds. In these compounds, heteroatoms participate in the formation of rings in addition to carbon atoms:



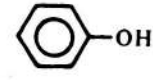
Furan Thiophene Pyrrole Pyridine

In a compound belonging to any of the above groups, the hydrogen atom can be replaced by a variety of atomic groups such as —OH, —NH_2, O O
‖ ‖
—C—H, and —C—OH. The introduction of such groups determines the chemical properties of the relevant molecules to a considerable extent, therefore they are called **functional groups** (chemical functions). A compound can contain several identical or different functional groups.

The presence of a specific functional group in organic molecules is the cause of the common nature of their properties, and this underlies their classification within each of the series. It should be noted that a substantial role in the manifestation of a specific function is played by the structure of a molecule's skeleton. For example, a hydroxy group can be bonded either to an aliphatic or to an aromatic radical (a hydrocarbon radical is a hydrocarbon residue containing an unpaired electron). In the first case, the compound will be an alcohol, and in the second, a phenol:

$$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2OH$$

Hexanol (alcohol)



Hydroxybenzene (phenol)

This example reveals that for an objective assessment of the properties of molecules, one must take into account the mutual influence of the atoms and atomic groups in a molecule.

Depending on the nature of the functional groups, we distinguish, for instance, alcohols (an OH group with an aliphatic radical, aldehydes (a $-\overset{\overset{O}{\|}}{C}-H$ group), acids (a $-\overset{\overset{O}{\|}}{C}-OH$ group), etc.

A **homologous series** is defined as *substances of one class similar in their structure and chemical properties, but differing from one another by one or more* CH_2 *groups.*

Questions and Problems

1. What features is the classification of organic substances based on? Compare it with the classification of inorganic compounds.
2. Explain the concepts "homologue" and "homologous series", "functional group". What is a heteroatom?

19.4. Classification and Mechanisms of Organic Reactions

Organic reactions can be classified in several ways depending on what criteria are chosen for this. These criteria include the change in the carbon skeleton, the nature of the reacting particles, the oxidation-reduction nature of the reagents, the addition or elimination of structural elements, and the kinetics of the reaction.

Each of these criteria enable one to single out groups of reactions having similar characteristics. The most general classification is that based on the addition or elimination of structural elements, according to which reactions of the following types are distinguished:

(1) displacement—an atom or group of atoms is removed from the initial molecule as a result of bond breaking, and a new atomic group is attached instead of it:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

(2) addition—atoms or groups of atoms combine with the carbon skeleton of the initial molecule:

$$CH_2{=}CH_2 + Br_2 \rightarrow \underset{\displaystyle Br}{\underset{|}{CH_2}}\!\!-\!\!\underset{\displaystyle Br}{\underset{|}{CH_2}}$$

$$CH_3{-}CH{=}CH_2 + HCl \rightarrow CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3$$

(3) elimination—the initial molecule detaches a group of atoms:

$$CH_3{-}CH_2{-}CH_2{-}CH_3 \xrightarrow[-2H_2]{} CH_2{=}CH{-}CH{=}CH_2$$

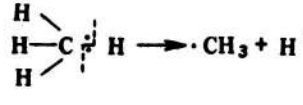
(4) regrouping (isomerization)

$$CH_2{=}CH{-}OH \rightarrow CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H$$

Each of the enumerated reactions can proceed according to a specific mechanism. The description of a chemical reaction by its steps is called a **mechanism**. Consequently, the mechanism of a reaction is the sequence of elementary steps through which the given reaction occurs. **Free-radical, electrophilic,** and **nucleophilic reactions** are distinguished.

An important criterion when determining the mechanism of a reaction is the type of chemical bond breaking in the initial molecule. **Homolytic** and **heterolytic** types of bond breaking are distinguished.

In **homolytic** bond breaking, particles form that have an unpaired electron and are called **radicals**. An example of such bond breaking is the formation of a methyl radical when methane reacts with chlorine:



In **heterolytic** bond breaking, electrically charged particles form. The bonding pair of electrons remains in one of the particles and it acquires a negative charge. The second particle separates in the form of a positive ion:

$$A:\!\!\mid B \longrightarrow A^+ + :B^-$$

$$H_3C-\overset{H}{\underset{H}{C}}\!\!\mid : I \longrightarrow C_2H_5^+ + :I^-$$

Particles that are charged negatively (e.g., OH^-, CN^-, I^-) or have a centre with an excess of electrons (e.g., oxygen in H_2O or nitrogen in NH_3) are called **nucleophilic**. Particles with a positive charge (e.g., H^+, NO_2^+, Br^+) or are deficient in electrons (e.g., the carbon in the group $>C=O$), are called **electrophilic**.

Now, knowing the nature of particle interaction and the type of bond breaking in an organic molecule, we can see what mechanism underlies displacement or substitution reactions.

A Molecule is Attacked by a Radical. Here homolytic breaking of a covalent bond occurs with the formation of new radicals. The initial radical reacts with one of the formed particles:

in the general form:

$$R:\!\!\mid X + \cdot R' \longrightarrow R^{\cdot} + R':X$$

For example:

$$Cl:\!\!\mid Cl \longrightarrow Cl\cdot + \cdot Cl$$

$$H_3C:\!\!\mid H + Cl\cdot \longrightarrow \cdot CH_3 + HCl$$

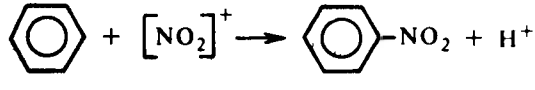
Such a substitution mechanism is designated by the symbol S_R—radical substitution.

A Molecule is Attacked by an Electrophilic Particle. Here heterolytic bond breaking occurs, and the particle (atom or group of atoms) being substituted separates in the form of a positive ion. The initial electrophilic particle combines with the formed anion:

in the general form:

$$A:\!\mid B + C^+ \rightarrow A:C + B^+$$

For example:



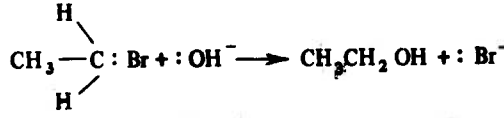
This substitution reaction is designated by the symbol S_E.

The Attacking Particle is a Nucleophilic One. Here heterolytic bond breaking also occurs, but the particle being substituted separates in the form of an anion.

in the general form:

$$A|:B+:C^- \rightarrow A:C+:B^-$$

For example:



Substitution reactions proceeding by this mechanism are designated by the symbol S_N.

In organic reactions, a carbon atom can form ions whose electric charge depends on which of the particles retains the electron pair when the bond is broken:

$$R|:X \rightarrow R^+ + :X^-$$
$$R:|X \rightarrow R:^- + X^+$$

When a carbon atom loses an electron, a positively charged particle known as a **carbocation** forms.

If when a bond is broken the common electron pair remains at a carbon atom, then the formed particle acquires a negative charge and is called a **carbanion.**

Questions and Problems

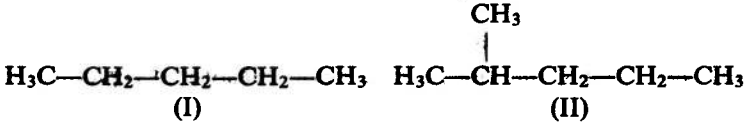
1. Compare the types of chemical reactions in organic and inorganic chemistry.
2. Explain what the symbols S_R, S_E, and S_N stand for.
3. Explain the essence of the concepts radical, nucleophil, electrophil, carbocation, and carbanion. What is the relation between them and the mechanism of a reaction?

19.5. Principles of Naming Organic Molecules

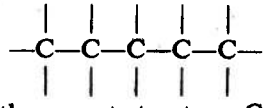
When studying organic chemistry, very great attention is given to questions of naming compounds, i.e. nomenclature. At present, the IUPAC (Geneva or substitutive) and radicofunctional systems are used.

In the IUPAC system, the one most favoured by organic chemists, two basic concepts are used, namely, the parent structure and the functional group.

By the parent structure is meant the main chain forming the basis of the given compound. It may be the chain of carbon atoms in an acyclic molecule, and a carboatomic or heterocyclic ring in a cyclic system. Let us consider two compounds as an example:



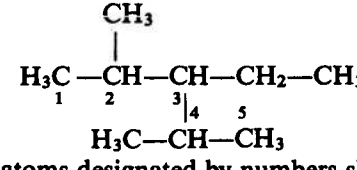
Compound (I) has an unbranched chain of carbon atoms and is pentane. If one hydrogen atom in a pentane molecule is substituted by a methyl radical (compound II), we obtain a different hydrocarbon containing six carbon atoms. Compound II should be considered as a derivative of pentane in which one hydrogen atom is substituted by a methyl group. Therefore, in compound II, the unbranched chain of carbon atoms (C_5), i.e.



should be considered as the parent structure. Compounds (I) and (II), as can be seen from their structures, relate to saturated hydrocarbons and, consequently, they have the same set of chemical properties. This is why we can assert that the introduction of a methyl group does not fundamentally affect the properties because the initial compound I was a hydrocarbon, and after the introduction of the methyl group a hydrocarbon formed again.

Let us consider specific examples of naming organic molecules using the IUPAC (substitutive) system.

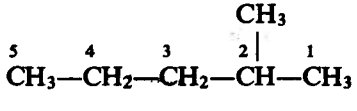
1. The parent structure is chosen so that account is taken of the maximum chain length, the maximum total number of double and triple bonds, and the maximum number of functional groups. For instance, in the structure



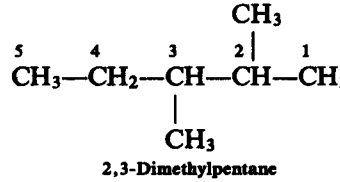
the chain of carbon atoms designated by numbers should be chosen as the parent structure because it has the maximum length and the largest number of branches.

2. After choosing the parent structure, the sequence of numbering is determined. This is done so that a branch is closer to the beginning of the chain.

3. Substituents are listed in alphabetic order by using prefixes with indication of their position in the parent structure. If a compound contains several identical substituents, their number is designated by the relevant Greek prefix (di-, tri-, tetra-, etc.):

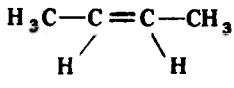


2-Methylpentane

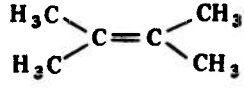


2,3-Dimethylpentane

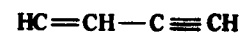
The radicofunctional system is used more rarely than the IUPAC one. It is based on choosing the simplest representative of a homologous series and then considering an entire compound as a derivative of this initial molecule. The following examples illustrate how compounds are named in this way:



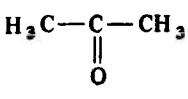
Dimethylethylene



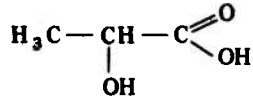
Tetramethylethylene



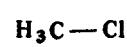
Vinylacetylene



Dimethylketone



Hydroxypropionic acid

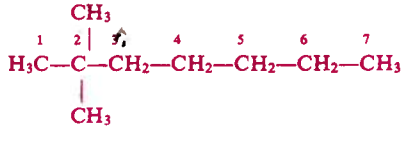


Methyl chloride

Notwithstanding the various nomenclature rules, there still exist some **trivial names** which the IUPAC committee on nomenclature recommends retaining. Their origin is often associated with the source of the relevant compound (e.g. butyric acid from rancid butter) or with other features. But these names do not in any way reflect the structural features of the organic molecules.

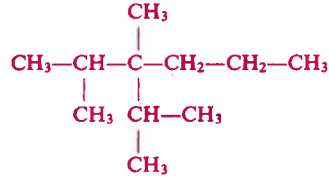
Questions and Problems

1. The hydrocarbon



can be named 2,2-dimethylheptane or trimethylpentylmethane. Which nomenclature system does each of these names correspond to?

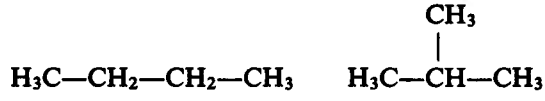
2. Indicate the parent structure in the formula



19.6. Kinds of Isomerism

The theory of chemical structure has created scientific prerequisites for explaining the phenomenon of isomerism. Research into the relation between the structure of molecules and their reactivity resulted in a further deeper cognition of this phenomenon. Several kinds of isomerism are distinguished, namely, (1) chain isomerism; (2) isomerism due to a different arrangement of substituents or of double or triple bonds; and (3) geometrical (*cis-trans*) isomerism *.

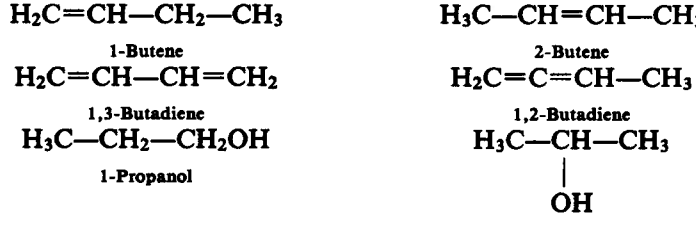
When considering the homologous series of methane, one can easily see that beginning from the fourth member, i.e. C_4H_{10}, isomerism of the carbon skeleton becomes possible. With a growth in the number of carbon atoms, the number of isomers grows. For instance, butane C_4H_{10} has two isomers:



Butane Isobutane

Pentane C_5H_{12} has three, heptane C_7H_{16} has nine, while the compound $C_{20}H_{42}$ (eicosane) has 366 319 isomers.

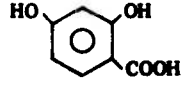
If a molecule contains double or triple bonds, they can occupy a different position in the carbon chain, therefore two or more substances with an identical structure of their carbon skeleton, but with a different arrangement of a double or triple bond are isomers. The same relates to compounds containing substituents because they can be bonded to different carbon atoms:



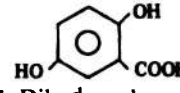
1-Butene 2-Butene

1,3-Butadiene 1,2-Butadiene

1-Propanol 2-Propanol



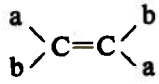
2,4-Dihydroxybenzoic acid



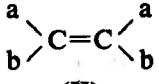
2,5-Dihydroxybenzoic acid

* We have listed the kinds of isomerism studied in a secondary school course of chemistry. Other kinds of isomerism are also known in organic chemistry.

If carbon atoms are joined by a double bond, substituents at these atoms can occupy different positions relative to the plane of the pi bond, which is shown conditionally below:



(I)



(II)

In structure (I), identical groups of atoms are at different sides of the pi-bond plane, therefore it is called a *trans*-isomer (Fig. 32). When identical groups of atoms are at the same side of the pi-bond plane, the structure is called a *cis*-isomer—structure (II).

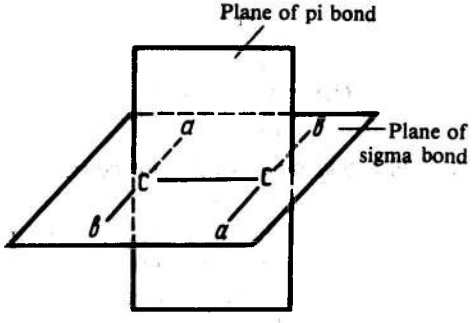
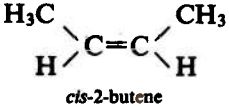


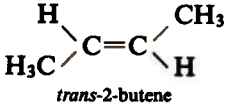
Fig. 32
Schematic view of a *trans*-isomer

This kind of isomerism is called **geometrical** or *cis-trans* isomerism. The existence of geometrical isomers is explained by the fact that a pi bond prevents the free rotation of atoms or groups of atoms along the axis of the sigma bond between two carbon atoms. One geometric isomer can transform into the other one only at high temperatures, under the action of ultraviolet radiation, etc.

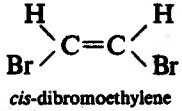
Geometrical isomers differ from each other in their properties:



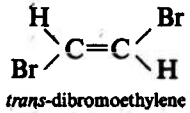
cis-2-butene
m.p. −139 °C
b.p. +4 °C



trans-2-butene
m.p. −105 °C
b.p. +1 °C

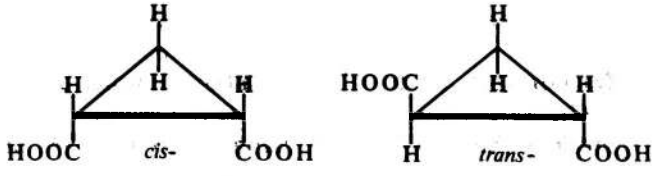


cis-dibromoethylene
m.p. −53 °C
b.p. +110 °C



trans-dibromoethylene
m.p. −6 °C
b.p. +108 °C

Geometrical isomerism is encountered not only in compounds with a double bond, but is also possible for alicyclic hydrocarbons, for example:



Cyclopropanedicarboxylic acid

The *cis*- and *trans*-isomers in the above example differ in the arrangement of the carboxyl groups and hydrogen atoms relative to the plane of the ring.

Questions and Problems

1. The concepts chain isomerism, isomerism of the position of substituents and of double or triple bonds, and geometrical (*cis-trans*) isomerism have been used in the present section. How do you understand this?
2. What is the difference between the concepts "homology" and "isomerism"?
3. We have two hydrocarbons:

$$CH_3-\underset{H}{C}=\underset{H}{C}-CH_2-CH_3 \qquad CH_3-\underset{H}{C}=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_3$$

Can they be considered as homologues? Isomers? Defend your answer.

19.7. Natural Sources of Organic Compounds. Petroleum Refining

Natural Gas. This is a convenient raw material for producing hydrocarbons with a low relative molecular mass. The major part of natural gas is methane (82-98%), the remainder being ethane, propane, and butane. The propane and butane are removed from the gas by liquefaction, after which it is delivered via gas pipelines to consumers. Large amounts of carbon black are also obtained from natural gas. It is used in the production of rubber for vehicle tyres. Numerous organic substances including some alcohols and acids are produced from the hydrocarbons contained in natural gas.

Petroleum. This very important raw material is a combustible mineral formed by a mixture of various hydrocarbons. The composition of petroleum depends on its origin, i.e. its place of occurrence. For example, crude petroleum from the island of Borneo is rich in aromatic hydrocarbons (about 39%), American mid-continental petroleum is rich in saturated

hydrocarbons, and Baku petroleum is rich in cycloalkanes (90%). In addition to hydrocarbons, petroleum includes about 10% of sulphur-, nitrogen-, and oxygen-containing compounds.

The **hydrocarbon fractions** contained in petroleum are separated by distillation.

The **gas fraction** (b.p. up to 40 °C) contains normal and branched alkanes up to C_5.

Petrol (gasoline) (b.p. 40-180 °C) contains up to 20% of C_6-C_{10} hydrocarbons. Over 100 individual compounds have been discovered in petrol, including normal and branched alkanes, cycloalkanes, and alkylbenzenes (arenes).

Paraffin oil (kerosene) (b.p. 180-230 °C) contains C_{11} and C_{12} hydrocarbons. It is mainly used as fuel.

Light gas oil (b.p. 230-305 °C) contains C_{13}-C_{17} hydrocarbons. It is used as a diesel fuel.

Heavy gas oil and **light lubricating oil distillate** (b.p. 305-405 °C) contain C_{18}-C_{25} hydrocarbons.

Lubricating oils (b.p. 405-515 °C) contain C_{26}-C_{38} hydrocarbons. The best known of these oils is petrolatum (vaseline).

The residue remaining after distillation is generally called **asphalt** or **tar.**

The main way of refining petroleum involves various kinds of **cracking,** i.e. the thermocatalytic conversion of the petroleum constituents. The following main kinds of cracking are distinguished.

Thermal cracking—hydrocarbons are fractionated under the action of high temperatures (500-700 °C). For example, a molecule of the saturated hydrocarbon decane $C_{10}H_{22}$ yields pentane and pentene molecules:

$$C_{10}H_{22} \rightarrow \underset{\text{Pentane}}{C_5H_{12}} + \underset{\text{Pentene}}{C_5H_{10}}$$

Catalytic cracking is also conducted at high temperatures, but in the presence of a catalyst, which makes it possible to control the process and conduct it in the required direction.

The cracking of petroleum yields unsaturated hydrocarbons that are widely used in the organic synthesis industry.

Coal Tar. This product is obtained in the coking of coal. The dry distillation of coal yields a **gas fraction** (coke gas), **coal tar,** and **coke.** The gas is composed of ammonia, hydrogen, carbon oxides, methane, ethylene (ethene), and other hydrocarbons.

Coal tar is a complicated mixture of hydrocarbons, oxygen- and nitrogen-containing substances and is separated by distillation into fractions with the following boiling ranges:

(1) up to 170 °C—light oil consisting mainly of hydrocarbons;

(2) 170-230 °C—middle oil with a considerable content of phenols;
(3) 230-270 °C—heavy oil; naphthalene is recovered from it;
(4) the residue—coal tar pitch.

Each of these fractions is additionally refined. The refined fractions are then distilled again.

Questions and Problems

1. What is the fundamental difference between the fractional distillation of petroleum and its cracking?
2. In what does coal tar differ from petroleum?

SUMMARY

Organic chemistry is the branch of chemistry studying carbon compounds. The scientific foundation of organic chemistry is formed by the theory of chemical structure that enables one to explain the relation between the structure and properties of molecules, and also to study the directions and mechanisms of organic reactions.

The diversity of organic compounds is explained by the features of structure of the carbon atom. It becomes possible to study the structure and properties of organic molecules owing to a harmonious classification system. Hydrocarbons are the simplest representatives of compounds of the aliphatic, alicyclic, and aromatic series. Substitution of hydrogen atoms in hydrocarbons by other atoms or groups of atoms (functional groups) yields various classes of organic compounds of a given series. Compounds containing the same functional group form a homologous series that is a series of substances differing from one another by any number of $-CH_2$ groups. A detailed description of a chemical reaction is called the mechanism of the reaction.

The mechanism of a given reaction depends on many factors, the most important of which are the nature of the reacting particles and the type of covalent bond breaking. Homolytic and heterolytic bond breaking are distinguished.

A carbocation is a particle carrying a positive charge chiefly localized on a carbon atom. A carbanion is a particle carrying a negative charge localized on a carbon atom.

Not only a radical, but also a nucleophil or electrophil can be a partner in a reaction.

Organic compounds are named in accordance with nomenclature rules, of which the substitutive system recommended by the IUPAC is the most popular among chemists. Its most important features are the parent structure and a functional group. The use of this system facilitates the studying

of organic molecules and creates prerequisites for bringing order into the terminology in different languages.

Organic molecules are characterized by isomerism—the existence of substances with an identical composition and molecular mass, but differing in their properties.

CHAPTER 20
HYDROCARBONS

OBJECTIVES

To know the main types of hydrocarbons and their distinctions; to know the names of the members of homologous series and the radicals they form; to know the structural features of alkanes, alkenes, and alkynes; to know the structure of benzene as the parent of the aromatic hydrocarbons; to know the chemical properties of the alkanes, alkenes, and alkynes; to study the mechanisms of reactions with the participation of saturated and unsaturated hydrocarbons and the mechanism of the reaction of electrophilic substitution in benzene; to know Markovnikov's rule and its application to addition reactions of alkenes and alkynes, and the orientation rules in the benzene ring.

20.1. Saturated Hydrocarbons (Alkanes)

Hydrocarbons are the simplest representatives of the aliphatic, alicyclic, and aromatic series.

Hydrocarbons are compounds whose molecules consist of atoms of two elements—carbon and hydrogen.

The aromatic hydrocarbons differ from the others in their structure and properties.

The compounds of the alicyclic series are close in their properties to aliphatic ones.

The saturated hydrocarbons include compounds in whose molecules the carbon atoms are only in the state of sp^3 hybridization and, consequently, are bonded only by sigma bonds. The alkanes have the general formula C_nH_{2n+2} and form a homologous series whose first ten members are described in Table 5.

Nomenclature and Isomerism. The names given in Table 5 have been recommended by the IUPAC as the main ones in its system of nomenclature.

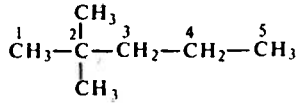
Table 5

The First Ten Members of the Homologous Series of Methane

Name	Formula	Melting point, °C	Boiling point, °C	Name of radical C_nH_{2n+1}	Formula of radical
Methane	CH_4	−184	−162	Methyl	CH_3
Ethane	C_2H_6	−172	−88	Ethyl	C_2H_5
Propane	C_3H_8	−187	−42	Propyl	C_3H_7
Butane	C_4H_{10}	−138	−0.5	Butyl	C_4H_9
Pentane	C_5H_{12}	−132	36	Pentyl	C_5H_{11}
Hexane	C_6H_{14}	−94.3	69	Hexyl	C_6H_{13}
Heptane	C_7H_{16}	−90	98	Heptyl	C_7H_{15}
Octane	C_8H_{18}	−56.5	124	Octyl	C_8H_{17}
Nonane	C_9H_{20}	−51	150.8	Nonyl	C_9H_{19}
Decane	$C_{10}H_{22}$	−32	174	Decyl	$C_{10}H_{21}$

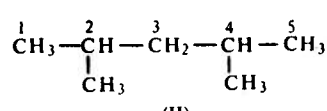
When studying isomers, one must know the names of organic radicals. They are formed from the name of the relevant hydrocarbon by changing the suffix *-ane* (alk*ane*) to *-yl* (alk*yl*), e.g. meth*ane*-meth*yl*, etc. (see Table 5). Radicals are generally designated by the capital letter R.

Let us consider a few examples:



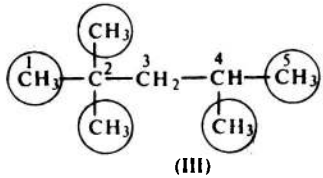
(I)

2,2-Dimethylpentane



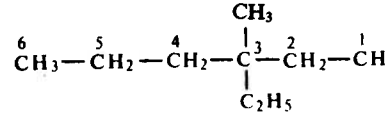
(II)

2,4-Dimethylpentane



(III)

2,2,4-Trimethylpentane



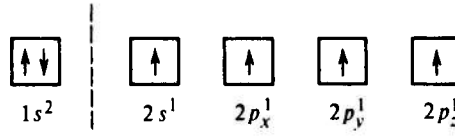
(IV)

3-Methyl-3-ethylhexane

It is convenient to classify every carbon atom in an alkane from the viewpoint of the number of other carbon atoms bonded to it. Compound (III) has carbon atoms of four different types. The atoms in the circles are bonded only to one carbon atom and are called **primary** ones. The atom designated by 3 (compound III) is bonded only to two other carbon atoms and is called a **secondary** one (the carbon atoms 2, 4, and 5 in compound IV are also secondary ones). If a carbon atom is bonded to three

other carbon atoms, it is called a **tertiary** one (carbon atom 4 in compound III, and atoms 2 and 4 in compound II). The carbon atoms 2 in compounds I and III and 3 in compound IV are bonded to four other carbon atoms, therefore they are called **quaternary** ones.

Structure of Alkanes. The electron configuration of a carbon atom in alkanes is $1s^2 2s^1 2p^3$. The formation of hybrid orbitals can be depicted in the form of the following scheme:



Four hybridized sp^3 orbitals

The carbon atoms in alkanes are bonded to one another by one sigma bond that forms as a result of the overlap of an sp^3 orbital of one carbon atom with the sp^3 orbital of another carbon atom. The axis of symmetry of this bond coincides with the straight line joining the nuclei of the carbon atoms. The sigma bond between atoms of carbon and hydrogen forms as a result of the overlap of the *s* orbital of hydrogen and the sp^3 orbital of carbon.

Figure 33 shows the formation of a methane molecule: the sp^3 hybrid orbitals are directed toward the apices of a tetrahedron. With such an arrangement, the orbitals are at the maximum distance from one another. For each of these orbitals to overlap with the *s* orbital of hydrogen the most effectively and form the most stable bond, the nucleus of each hydrogen atom must be at an apex of the tetrahedron.

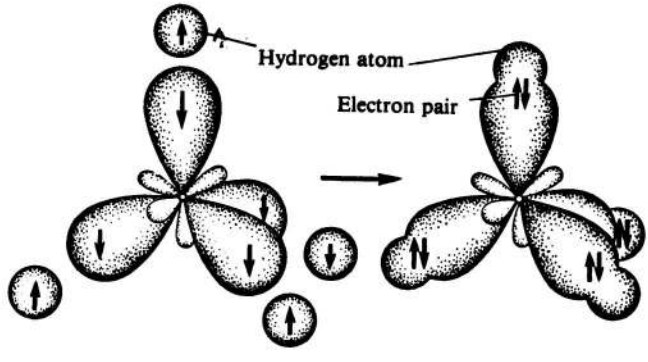


Fig. 33
Formation of a methane molecule

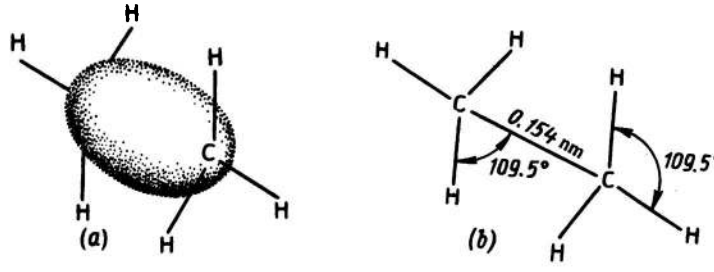


Fig. 34
An ethane molecule:
a—simple carbon-carbon bond (sigma bond); *b*—shape and dimensions

In ethane, the length of the C—C bond is 0.154 nm, of the C—H bond is 0.110 nm, and the bond angle is 109.5 °C (Fig. 34).

It is important to stress that the carbon atoms in a chain can rotate about the C—C bonds similar to rotation about an axis. Therefore, a chain can alter its configuration in space. This is especially important for chains with many members.

The features of alkane structure, namely, the presence of stable covalent bonds (sigma bonds) with a low polarizability, characterize the reactivity of these compounds. Alkanes mainly enter into reactions proceeding by an S_R mechanism. At sufficiently high temperatures, a carbon-carbon bond breaks (the cracking process).

Physical Properties. Hydrocarbons containing from one to four carbon atoms are gases, from five to 17 atoms are liquids, and over 17 atoms are solids.

With an increase in the chain length by one carbon atom, the boiling point of hydrocarbons grows by 20-30 K, except for methane, ethane, and propane. Normal alkanes (with a straight chain) boil at a higher temperature than their branched-chain isomers. Alkanes are not polar and are therefore virtually insoluble in water, but dissolve well in non-polar and slightly polar organic solvents. In the pure form, they are colourless and have a weak odour.

Chemical Properties. The displacement reactions most typical of alkanes (halogenation, nitration, sulphurization) proceed by a radical mechanism. These reactions require sufficiently rigid conditions. For instance, a free atom or radical forms in the thermal decomposition of a molecule of one of the reactants.

Let us consider in detail the chlorination of methane. It can be represented as a sequence of displacement reactions:

$$CH_4 + Cl_2 \rightarrow \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \rightarrow \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow \underset{\substack{\text{Trichloromethane}\\(\text{chloroform})}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \rightarrow \underset{\substack{\text{Carbon}\\\text{tetrachloride}}}{CCl_4} + HCl$$

The process occurs vigorously in the light or at a sufficiently high temperature (250-400 °C). A chlorine molecule breaks up into two atoms (homolytic bond breaking). This step is called **chain initiation** because the formed radicals further call forth a sequence of reactions proceeding by an S_R mechanism:

$$Cl{:}Cl \xrightarrow[\text{or light}]{\text{heating}} Cl\cdot + Cl\cdot \qquad \text{Chain initiation}$$

$$\left.\begin{aligned} &CH_4 + Cl\cdot \rightarrow \cdot CH_3 + HCl\\ &\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot\\ &\cdot Cl + CH_3Cl \rightarrow \cdot CH_2Cl + HCl\\ &\cdot CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + \cdot Cl \end{aligned}\right\} \text{Chain propagation}$$

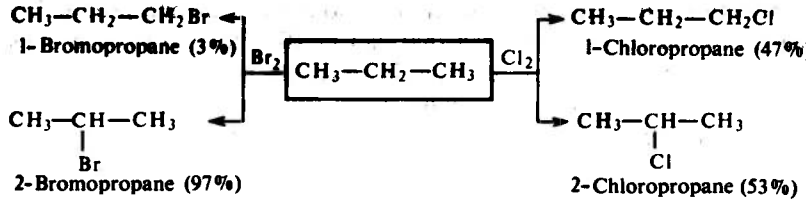
A different process is also possible, namely, **chain termination:** two methyl radicals combine to form ethane, and two chlorine atoms combine into a Cl_2 molecule:

$$\left.\begin{aligned} &\cdot CH_3 + \cdot CH_3 \rightarrow H_3C{-}CH_3\\ &\cdot Cl + \cdot Cl \rightarrow Cl_2 \end{aligned}\right\} \text{Chain termination}$$

The process of halogenation relates to **chain reactions** *. Reactions similar to those described above for chlorine occur when methane reacts with fluorine and bromine, the reactivity of the halogens increasing from bromine to fluorine. The reaction with fluorine proceeds with an explosion in the dark at room temperature, therefore it is conducted in the cold and in the presence of a noble gas.

Alkanes react with bromine with a high selectivity, therefore one isomer generally forms. Hence, the structure of the products is determined by the structure of both the initial alkane and the halogen:

* An important contribution to the studying of chain reactions was made by N. Semenov, who was awarded the Nobel Prize for his work.



The alkanes enter into a nitration reaction by the radical mechanism. Under ordinary conditions, nitric acid does not react with alkanes, but when the reaction mixture is heated to 140 °C and is at a high pressure, dilute HNO_3 plays the role of the nitrating agent. A hydrogen atom in alkanes is substituted by a nitrogroup $-NO_2$, and a nitroderivative forms. Here the nitric acid decomposes with the formation of two particles each having an unpaired electron:

$$HNO_3 \rightleftarrows HO\cdot + \cdot NO_2$$

Next substitution occurs by the S_R mechanism:

$$CH_4 + \cdot OH \rightarrow \cdot CH_3 + H_2O$$
$$CH_3 + HNO_3 \rightarrow CH_3NO_2 + HO\cdot$$

Alkanes generally decompose into carbon and hydrogen at a temperature above 1000 °C:

$$CH_4 \rightarrow C + 2H_2$$

By changing some of the reaction parameters, however, the process can be monitored so that intermediates can be isolated. An example is the decomposition of methane with the formation of acetylene, which is widely used in the industry. This process is called **methane cracking:**

$$2CH_4 \rightarrow HC{\equiv}CH + 3H_2$$

Higher hydrocarbons decompose to form a mixture of saturated and unsaturated compounds:

$$C_mH_{2m+2} \rightarrow C_nH_{2n+2} + C_pH_{2p}$$

where $m = n + p$.

Alkane oxidation reactions generally proceed at high temperatures. They are attended by breaking of carbon-carbon bonds and by the formation mainly of acids.

The oxidation of the lower alkanes proceeds much more difficultly.

Hydrocarbons burn in the air or in a stream of oxygen to form water and carbon dioxide. A considerable amount of energy is evolved. This allows them to be used as a gaseous fuel, e.g. natural gas (methane):

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$$

Production. In addition to the natural sources of alkane production, numerous synthetic ways are used that can be divided into three groups.

The first group consists of reactions in which the reactants and products contain the same number of carbon atoms. Examples are:

(a) the hydrogenation of unsaturated hydrocarbons:

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + 2H \rightarrow \underset{\text{Ethane}}{H_3C{-}CH_3}$$

(b) the reduction of halogen derivatives using hydrogen or hydrogen iodide:

$$CH_3I + 2H \rightarrow CH_4 + HI$$
$$CH_3I + HI \rightarrow CH_4 + I_2$$

The second group includes reactions in which the product contains more carbon atoms than the reactant. Special mention should be made here of the reaction of halogen derivatives with metallic sodium:

$$\underset{\text{Iodoethane}}{C_2H_5I} + 2Na + \underset{\text{Iodoethane}}{IC_2H_5} \longrightarrow \underset{\text{Butane}}{C_4H_{10}} + 2NaI$$

The third group includes reactions in which the product contains less carbon atoms than the reactant:

$$\underset{\text{Sodium acetate}}{CH_3C(=O){-}ONa} + NaOH \xrightarrow{\text{fusion}} CH_4 + Na_2CO_3$$

Methane can be synthesized:

(a) directly from carbon and hydrogen:

$$C + 2H_2 \rightarrow CH_4$$

(b) by the thermocatalytic reduction of the carbon oxides CO and CO_2:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

At a laboratory, methane can be prepared by fusing sodium acetate with dry sodium hydroxide.

Application. Methane is contained in large amounts in natural gas. Illuminating gas contains about 34-35% of methane in addition to hydrogen, carbon monoxide, unsaturated hydrocarbons, nitrogen, and carbon dioxide.

Methane is widely used in industry. It is transformed chemically into acetylene, fluoro- and chloroderivatives. The chemism of these processes has been treated above.

Questions and Problems

1. Disclose the essence of the following concepts: alkane, sp^3 hybridization, chain reaction, halogenation, and nitration.

2. Write the formula of a saturated hydrocarbon containing (a) only primary carbon atoms in the chain; (b) primary and secondary carbon atoms; (c) primary and tertiary carbon atoms; (d) primary and quaternary carbon atoms; (e) primary, secondary, and tertiary carbon atoms; and (f) primary, secondary, tertiary, and quaternary carbon atoms. Name the hydrocarbons whose formulas you have written using the IUPAC nomenclature.

3. How can the transformation $CH_4 \rightarrow CH_3—CH_3$ be carried out?

4. Explain the nature of the sigma bond between carbon atoms.

5. Use the examples of methane and butane to show how the type of hybridization of a carbon atom affects the geometry of a molecule.

6. Write the possible isomers of the hydrocarbon C_5H_{12} and name them using the IUPAC nomenclature.

7[a]. What volume of oxygen is consumed in the combustion of 100 lit of a gas mixture containing 65% of methane, 15% of ethane, and 5% of hydrogen?

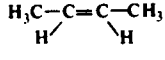
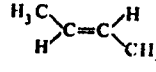
8[a]. A fluorine derivative of a hydrocarbon has a density relative to hydrogen of 33. The composition of this compound is 36.36% of C and 57.57% of F (the remainder being hydrogen). Determine the molecular formula of the compound.

20.2. Ethylene Hydrocarbons (Alkenes)

The members of this series have the general formula C_nH_{2n} and are characterized by the presence of one double bond between any two adjacent carbon atoms. The double (pi) bond is formed with the participation of sp^2 hybridized carbon atoms. The parent of the homologous series of alkenes (Table 6) is ethylene (ethene).

Table 6

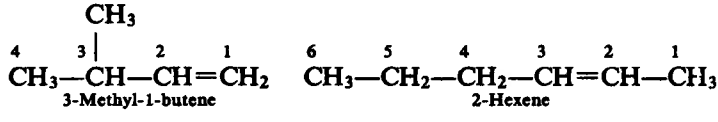
First Three Members of the Ethylene Series

Name		Formula	Structure	M.p., °C	B.p., °C
Trivial	IUPAC				
Ethylene	Ethene	C_2H_4	$H_2C=CH_2$	−169	−102
Propylene	Propene	C_3H_6	$H_3C—CH=CH_2$	−185	−48
Butylene	**Butenes:**	C_4H_8			
	1-butene		$H_3C—CH_2—CH=CH_2$	−130	−6
	cis-2-butene			−139	+4
	trans-2-butene			−106	+1

Nomenclature and Isomerism. By the IUPAC (substitutive) nomenclature, the names of these hydrocarbons are derived from the relevant alkane by changing the suffix *-ane* to *-ene*.

Isomerism in the alkene series depends on chain isomerism, the position of the double bond, and also on the arrangement in space of the identical atoms or groups of atoms at the carbons joined by the double bond (*cis-trans* isomerism).

When an alkene has more than three carbon atoms, a prefix number must be used to indicate the position of the double bond. The chain is numbered starting at the end closer to the double bond. The number of the carbon atom at which the double bond begins is used as the prefix number:



The geometrical isomerism of alkenes is shown in Table 6 using 2-butene as an example.

Structure of Alkenes. The distinguishing feature here is the double carbon-carbon bond. The carbon atoms joined by a double bond are in the state of sp^2 hybridization: one *s* and two *p* orbitals combine to form three hybrid orbitals (Fig. 35). They are in the plane of an equilateral triangle, therefore the angles between them are 120°. The third *p* orbital not participating in the hybridization remains unchanged and is at right angles to the plane of the hybridized orbitals:

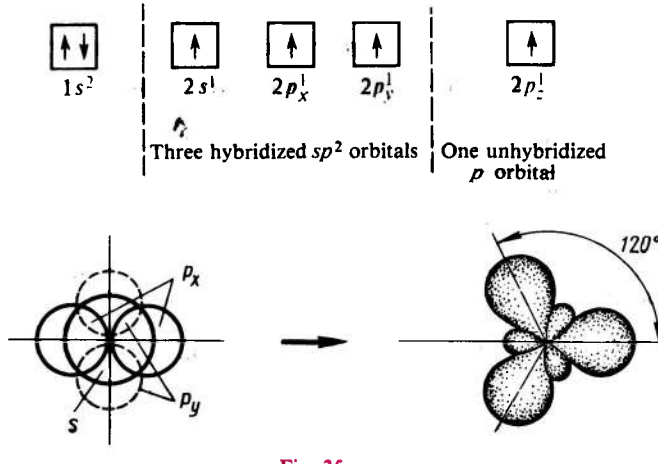


Fig. 35
Formation of three hybrid sp^2 orbitals

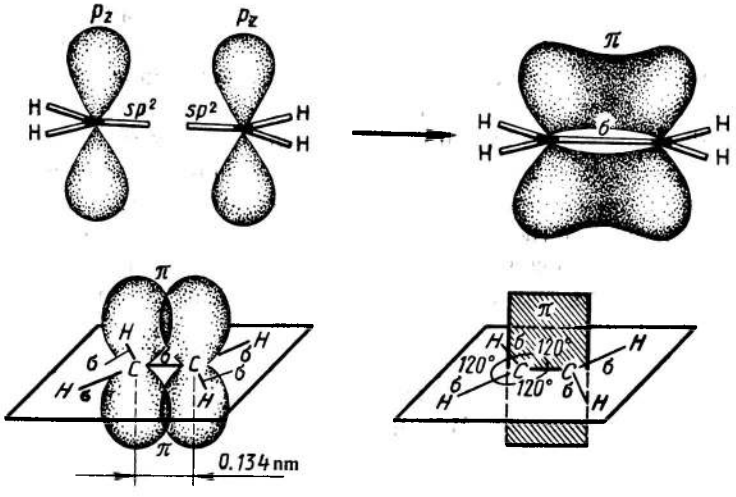


Fig. 36
Structure of the ethylene bonds

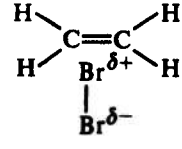
When forming a double bond, the hybridized orbitals of each carbon atom form ordinary sigma bonds (one C—C and two C—H bonds). The unhybridized *p* orbital of one carbon atom overlaps with a *p* orbital of the second carbon atom. This "sideways" overlap results in the formation of another bond (a pi bond) that is in a plane at right angles to the sigma bond (Fig. 36). The length of the carbon-carbon bond in this case is 0.134 nm.

The energy needed to break a single carbon-carbon bond is about 352 kJ/mol, while for a double C=C bond it is 587 kJ/mol. The strength of the pi bond is 587 − 352 = 235 kJ/mol, which is considerably smaller than that of a sigma bond (compare 352 and 235 kJ/mol). The explanation is that a bond formed with sideways overlap (a pi bond) is weaker than with head-on overlap (a sigma bond). The electrons participating in pi bonding are retained more weakly by the carbon nuclei, therefore the polarizability of this bond is much higher than of a sigma bond. The cloud of pi electrons of the double bond is over and under the plane of the sigma bond, which ensures their greater accessibility for attacking.

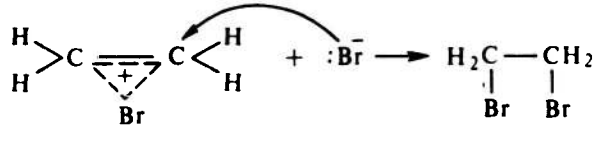
Physical Properties. The lower homologues of the alkenes are gases under ordinary conditions, while beginning with pentene C_5H_{10} they are low-boiling liquids. The alkenes, like the alkanes, are practically insoluble in water, but are soluble in non-polar organic solvents. The properties of the first three alkenes are given in Table 6.

Chemical Properties. In many reactions, the pi bond is a donor of electrons, therefore it reacts readily with electrophilic reagents. In this connection, the most typical reactions of alkenes are **electrophilic addition:** the pi bond breaks by a heterolytic mechanism. If the attacking particle is a radical, the bond breaks by a homolytic mechanism and then **free-radical addition** occurs. Also typical of alkenes are pi-bond **oxidation reactions.**

Halogenation. The mechanism of a halogenation reaction includes an electrophilic attack of the pi electrons by a halogen molecule. The attacking molecule, e.g. Br_2, does not have its own dipole, but a dipole is **induced** near the pi electrons, and this is why a halogen behaves like an electrophilic agent:

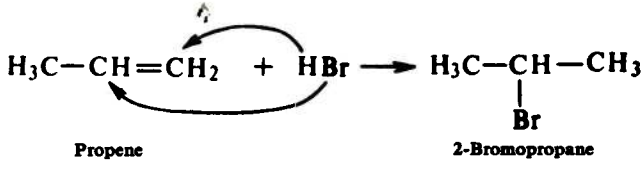


Under its influence, the pi bond becomes polarized, and conditions are created for the addition of bromine atoms to each carbon atom (electrophilic addition). The product formed is dibromoethane:



Addition of Hydrogen Halides (Hydrohalogenation). Molecules of hydrogen halides combine with alkenes to form alkane halides. The reaction proceeds in accordance with **Markovnikov's rule:**

hydrogen adds to the more hydrogenated carbon atom at the double bond:



Propene 2-Bromopropane

To explain Markovnikov's rule, let us consider the distribution of the electron density in propene whose molecule has sp^3 and sp^2 hybridized carbon atoms. The type of hybridization affects the electronegativity, which changes in the following sequence:

$$C_{sp} > C_{sp^2} > C_{sp^3}$$

This is why the electron density is displaced from the methyl group (C_{sp^3})

toward the double bond, which can be shown by arrows:

$$CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2$$

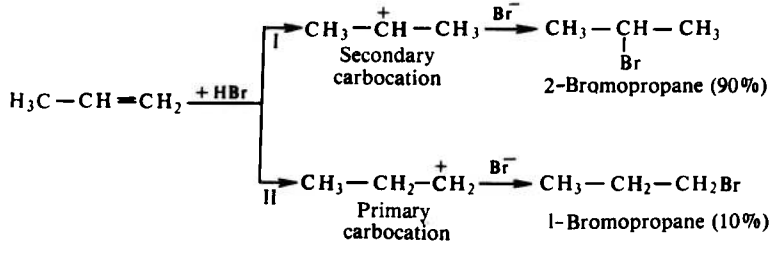
The symbols $\delta+$ and $\delta-$ show the deficiency and surplus of electron density on the section of the C=C bond in propene. The methyl group displaces the electron density along the sigma bond toward the CH group.

The shift of the electron density along a sigma bond in a molecule under the influence of atoms or atomic groups is called the inductive effect.

This effect is considered to be positive (a $+I$ effect) when an atom or atomic group facilitate the shift of the electron density in the direction of a carbon atom. The atom H and the group $-CH_3$ have such properties.

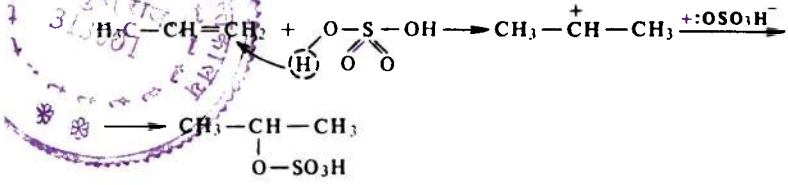
If an atom or group of atoms withdraw the electrons of a sigma bond from carbon atoms toward themselves, we have a negative inductive effect (a $-I$ effect). The halogens, sp^2 and sp hybridized carbon atoms have such an effect. This enables us to state that the shift of the electron density in propene shown above will facilitate the donation of a proton from HBr to the CH_2 group. This approach to explaining the process is only the result of taking into account the static factors depending on the different electron density and the partial charge on the carbon atoms at the double bond. The dynamic (or kinetic) factor is the other important one. It manifests itself directly in the course of a reaction and takes into consideration the stability of the intermediate particles.

The reaction of addition of hydrogen bromide to propene can proceed in two directions:



The first direction is more preferable owing to the nature of the formed carbocation (carbonium ion) at the secondary carbon atom. The positive charge on the carbon atom here is suppressed much more strongly by the $+I$ effect of the two methyl radicals than in the primary carbocation in the second direction of this reaction, where the charge is suppressed by only one radical. Consequently, the carbocation is more stable when the process follows the first direction.

Alkenes add sulphuric acid to form alkyl sulphates:



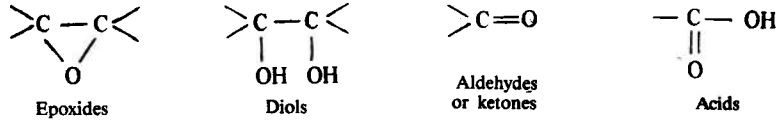
If the product is reacted with water, an alcohol forms:

$$CH_3-\underset{\displaystyle O-SO_3H}{\underset{|}{CH}}-CH_3 + H_2O \rightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

This explains why alkenes add water in the presence of sulphuric acid (hydration), the product being an alcohol. This reaction is widely used in the industry to produce ethanol:

$$\underset{\text{Ethylene}}{CH_2=CH_2} + HOH \xrightarrow{H_2SO_4} \underset{\text{Ethanol}}{C_2H_5OH}$$

Alkene Oxidation Reactions. These reactions generally proceed readily and depending on the oxidizing agent and the conditions of a reaction, they are attended either only by the breaking of a pi bond, or of a pi and sigma bonds simultaneously. Possible products are:



For example, when ethylene is passed through a solution of $KMnO_4$, a diatomic alcohol—1,2-ethanediol (ethylene glycol) forms. The solution loses its colour, therefore this reaction is used as a qualitative one to identify double carbon-carbon bonds:

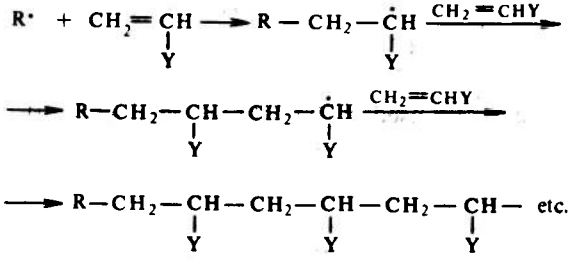
$$3CH_2=CH_2 + 2KMnO_4 + 4H_2O \rightarrow 2KOH + 2MnO_2 + 3\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

Addition of Hydrogen—Hydrogenation. Alkenes react with hydrogen in the presence of metallic catalysts (Pt, Pd, or Ni) with the formation of alkanes:

$$CH_2=CH_2 + H_2 \rightarrow CH_3-CH_3$$

Polymerization Reactions. These are reactions of the consecutive addition of several alkene molecules to one another as a result of breaking of

the double bond. The formed **polymer** is a **macromolecule** consisting of a large number of repeating units. Polymerization can follow various mechanisms. The free-radical (chain) mechanism presumes an attack by a radical and the subsequent homolytic breaking of a pi bond. The radical formed in the second step now attacks a second alkene molecule, and so on. These reactions are catalyzed by substances such as peroxides capable of forming free radicals. A polymerization reaction can be represented as follows:



Ethylene polymerizes as shown below:

$$H_2C{=}CH_2 + CH_2{=}CH_2 + CH_2{=}CH_2 + \ldots + CH_2{=}CH_2 \rightarrow$$

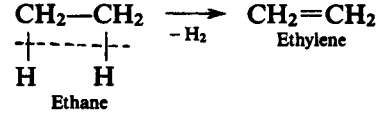
$$\rightarrow\ldots{-}H_2C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\ldots\rightarrow$$

$$\rightarrow[{-}CH_2{-}CH_2{-}]_n$$

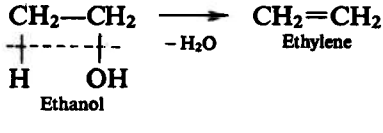
Polyethylene

The part $-CH_2-CH_2-$ of the polymer is called its **structural unit.** A molecule of the initial alkene is called a **monomer.** When two monomers combine, the product is a **dimer,** when three combine, it is a **trimer,** etc.

Production of Alkenes. Alkenes can be produced by a reaction of catalytic dehydrogenation (the removal of hydrogen) of the relevant saturated hydrocarbons:



or from the relevant alcohols by a dehydration reaction (the removal of water). Catalysts such as H_2SO_4, $AlCl_3$, and H_3PO_4 are used in these reactions:



Alkenes can also be produced from monohalogen derivatives of alkanes by a reaction with an alcohol solution of an alkali (a dehydrohalogenation reaction):

$$\underset{\text{Ethyl chloride}}{CH_3—CH_2Cl} + KOH \xrightarrow{\text{alcohol}} \underset{\text{Ethylene}}{CH_2=CH_2} + KCl + H_2O$$

or from dihalogen derivatives of alkanes by a reaction, for example, with zinc

$$\underset{\text{Dichloroethane}}{\begin{matrix} CH_2—CH_2 \\ | \quad | \\ Cl \quad Cl \end{matrix}} + Zn \rightarrow \underset{\text{Ethylene}}{CH_2=CH_2} + ZnCl_2$$

Alkenes are widely used in the national economy in the production of halogen derivatives (e.g., dichloroethane), alcohol (ethanol from ethylene), of various polymers, etc. Figure 37 shows the industrial applications of ethylene.

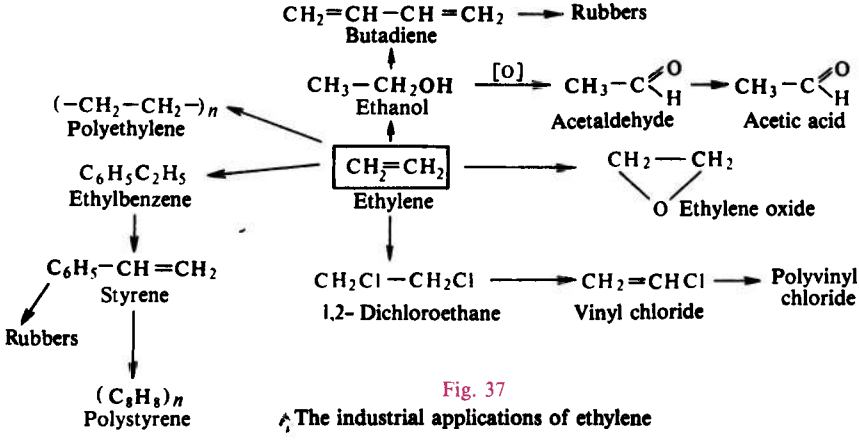


Fig. 37
The industrial applications of ethylene

Questions and Problems

1. Explain the electron mechanism of hydrogen halide addition by Markovnikov's rule.
2. Why is geometrical isomerism possible for alkenes?
3. What is the difference between a monomer and a structural unit, between a monomer and a polymer?
4. What is the difference between ethane and ethylene? Defend your answer.
5. Explain the mechanism of adding halogens to alkenes using 1-butene as an example.
6. Explain the electron mechanism of addition of hydrogen chloride to 1-butene by Markovnikov's rule.
7[a]. Write the equation of the reaction of propene with hydrogen and calculate by how much the volume of the gas mixture will decrease after completion of the reaction.

8[a]. Determine the formula of an alkene if 0.4 g of it adds 1.143 g of bromine.

9[a]. When 20 lit of a mixture of ethane and ethylene were passed through liquid bromine, the mass of the flask increased by 7 g. What was the composition (in per cent by volume) of the initial mixture?

10[a]. A reaction of zinc with hydrochloric acid evolved a volume of hydrogen that was sufficient for the complete hydrogenation of 2.24 lit of ethylene. How many grammes of zinc reacted and what volume of hydrogen formed?

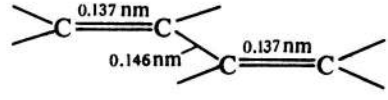
11[a]. The combustion of 1.4 g of a hydrocarbon yielded 4.4 g of CO_2 and 1.8 g of H_2O. The density of this substance relative to hydrogen is 28. Determine the true formula of the hydrocarbon and write its possible structural isomers.

20.3. Dienes. Rubbers

Compounds of this series are characterized by the presence of two double bonds and have the general formula C_nH_{2n-2}.

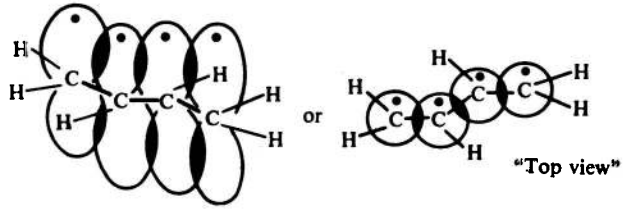
Nomenclature and Isomerism. By the IUPAC nomenclature, dienes are named like alkenes, except that the suffix *-ene* is changed to *-adiene* ($CH_2=CH-CH=CH_2$ is but*adiene*). The structural isomerism is determined by the structure of the carbon skeleton and the position of the double bonds.

Structure of Dienes. The studying of dienes, and especially of butadiene, made it possible to establish the following structure of the latter (1,3-butadiene)



The length of the bonds between C_1 and C_2, C_3 and C_4 exceeds somewhat that of the double bond in ethylene (0.134 nm), while the bond length between C_2 and C_3 is 0.146 nm, which is considerably smaller than the length of a single carbon-carbon bond in alkanes (0.154 nm).

All the atoms in butadiene are in one plane, and the bond angles are 120°. The pi bonds are in a plane at right angles to the one accommodating all the atoms. This is a result of the fact that the *p* orbitals overlap not only between C_1 and C_2, C_3 and C_4, but also partly between the second and third carbon atoms as shown below:



Hence, a single pi-electron cloud forms in **conjugated** dienes, i.e. dienes in which the pi bonds are separated from each other by a single sigma bond:

$$H_2C{=}CH{-}CH{=}CH_2$$

This feature of conjugated dienes determines their reactivity. Being unsaturated, they enter into an addition reaction by the electrophilic or radical mechanisms.

Polymerization. The polymerization of dienes proceeds mainly with the formation of polymers identical or similar to natural rubber (caoutchouc):

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH{-}CH{=}CH_2 + \ldots$$
$$\ldots + CH_2{=}CH{-}CH{=}CH_2 \rightarrow (-CH_2{-}CH{=}CH{-}CH_2-)_n$$

Natural Rubber (Caoutchouc). In the 16th century, Spaniards who landed in South America gave attention to the balls which the Indians were using in their games. These balls were made from an elastic and soft substance unknown in Spain and produced by the Indians from the milky juice of a tree called the hevea. The Indians used this substance to make waterproof footwear or treated fabric with it to make the fabric waterproof. The local inhabitants called the hevea juice "caoutchou", whence the name caoutchouc originated.

Studying of the properties of natural rubber showed that when it is heated, it begins to decompose with the formation of an oily substance—isoprene. When isoprene was polymerized in the presence of hydrochloric acid, rubber was obtained. These data showed that natural rubber should be considered as a polymer based on isoprene.

Very few countries have sources of natural rubber, and they cannot meet the world's growing demand for this valuable product. This is why the establishment of the structure of natural rubber gave a major impetus to research aimed at creating synthetic rubber.

In 1932, synthetic rubber was produced for the first time in the world from butadiene by the Soviet chemist, Academician S. Lebedev. Being a pioneer in the production of synthetic rubber, the Soviet Union already in 1936 occupied the first place in the world in the volume of its production.

At present, the following compounds based on dienes are widely used for many purposes.

A rubber consisting of 80% of 1,3-butadiene and 20% of styrene $C_6H_5{-}CH{=}CH_2$ is widely used in the manufacture of motor vehicle tyres and rubber articles. If the styrene is replaced with acrylonitrile $CH_2{=}C{-}{-}CN$, the product acquires resistance to the dissolving effect of petrol and oils.

Synthetic rubber based on chloroprene (2-chloro-1,3-butadiene) resists effects of the weather and of various oils. It is not combustible.

Rubbers based on isoprene (2-methyl-1,3-butadiene) are close in their properties to the natural product.

To reduce the plasticity of rubber and improve its strength, wear resistance and resistance to aggressive media, it is subjected to **vulcanization**—heating in the presence of sulphur with various fillers (carbon black, chalk, zinc oxide, etc.). During the vulcanization process, the rubber molecules become "cross-linked" by disulphide (—S—S—) bridges and form a three-dimensional polymer—**vulcanized rubber.**

To produce a synthetic rubber, two essential conditions must be observed, namely, (1) the formation of a polymer unbranched chain must be ensured, and (2) the polymerization process must be controlled so as to retain the spatial features of the relevant *cis-trans* isomers.

For example, natural rubber is an isoprene polymer in which the fragments of the polymer chain at each double bond are in the *cis*-position. Another natural polymer of isoprene—gutta-percha—differs from natural rubber in that the fragments of the polymer chain at the double bonds in it are in the *trans*-position. Natural rubber is elastic, while gutta-percha is not.

Consequently, the difference in the properties of these two isoprene polymers is due to the different arrangement of the fragments at the double bond in space. This feature is called **stereoregularity.**

Questions and Problems

1. Disclose the meaning of the concepts dienes, conjugation, vulcanization, and stereoregularity.
2. Write the structural formulas of chloroprene and isoprene in accordance with their IUPAC names given in the text.
3. Explain the polymerization of chloroprene and isoprene. Write the reaction equations.
4. Explain the copolymerization of butadiene and styrene. Write the reaction equation.
5. Indicate the similar and different features of the structure of butadiene, butene, and butane.

20.4. Acetylene Hydrocarbons (Alkynes)

The hydrocarbons of this series have the general formula C_nH_{2n-2} and are featured by the presence in a molecule of two *sp* hybridized carbon atoms joined by two pi bonds in addition to a sigma bond.

An alkyne molecule contains four hydrogen atoms less than the corresponding alkane molecule.

Acetylene is the parent of the homologous series, the first three members of which are indicated in Table 7.

Nomenclature and Isomerism. When writing the names of these hydrocarbons according to the IUPAC nomenclature, the same rules as for the alkenes are followed, except that the suffix *-yne* is used instead of *-ene*

Table 7

First Three Members of the Alkynes

Name		Formula	Structure	M.p., °C	B.p., °C
Trivial	IUPAC				
Acetylene	Ethyne	C_2H_2	$HC{\equiv}CH$	−82	−84
Methyl-acetylene	Propyne	C_3H_4	$H_3C{-}C{\equiv}CH$	−102	−23
	Butynes:				
Ethylacet-ylene	1-Butyne	C_4H_6	$CH_3{-}CH_2{-}C{\equiv}CH$	−122.5	−8.5
Dimethyl-acetylene	2-Butyne		$H_3C{-}C{\equiv}C{-}CH_3$	−32.5	27

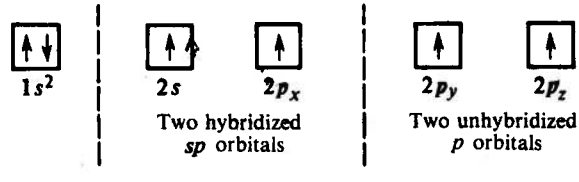
(eth*ene*-eth*yne* C_2H_2, prop*ene*-prop*yne* C_3H_4, but*ene*-but*yne* C_4H_6, etc.). Isomerism in the alkynes depends on the isomerism of the carbon chain and on the position of the triple bond:

$\overset{5}{C}H_3{-}\overset{4}{C}H_2{-}\overset{3}{C}H_2{-}\overset{2}{C}{\equiv}\overset{1}{C}H$ 1-pentyne

$\overset{5}{C}H_3{-}\overset{4}{C}H_2{-}\overset{3}{C}H{\equiv}\overset{2}{C}H{-}\overset{1}{C}H_3$ 2-pentyne

$\overset{4}{C}H_3{-}\overset{3}{C}H(\overset{1}{C}H_3){-}\overset{2}{C}{\equiv}\overset{1}{C}H$ 3-methyl-1-butyne

Structure of Alkynes. The electron structure of a carbon atom at a triple bond can be represented as follows:



The carbon atoms, being *sp* hybridized (Fig. 38), are joined by a triple bond, namely, one sigma and two pi bonds. Two hybridized *sp* orbitals (one from each carbon atom) overlap to form a sigma bond (head-on overlap). The unhybridized *p* orbitals ($2p_y$ and $2p_z$) remaining at each carbon atom are in mutually perpendicular planes and overlap respectively with the similar orbitals of the other *sp* hybridized carbon atom to form two pi bonds (sideways overlap). These two pi bonds are in planes at right angles to each other and to that of the sigma bond (Fig. 39).

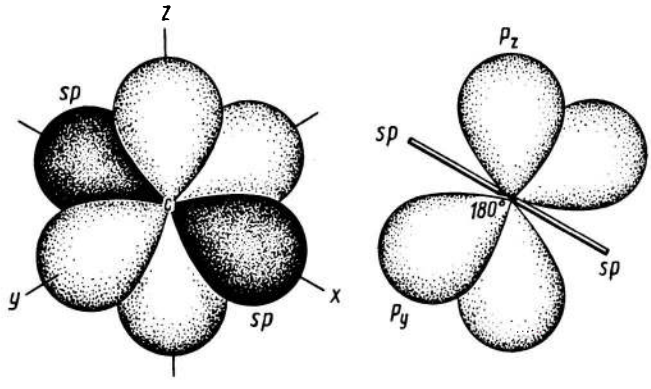


Fig. 38
The *sp* hybridization of a carbon atom

The length of the carbon-carbon bond is 0.120 nm, and the bond angles equal 180°, i.e. the acetylene molecule is linear.

Acetylene and its homologues are still more unsaturated than the alkenes, therefore we have all the grounds to expect that these hydrocarbons should first of all enter into an addition reaction. The presence of two pi bonds indicates that in comparison with the alkenes, they add two moles of a reagent (e.g., one mole of H_2, Br_2, or HBr per pi bond).

Attention should be given to another important feature of alkynes, i.e. the presence in some of them of a hydrogen atom at an *sp* hybridized carbon atom ≡C—H (compare 1-butyne $CH_3—CH_2—C{\equiv}CH$ and 2-butyne $CH_3—C{\equiv}C—CH_3$). As indicated previously, the electronegativity of an *sp* hybridized carbon atom is much higher than in an sp^2 or sp^3 hybridized one. Consequently, in the series of compounds

$$H_3C—CH_3;\quad H_2C{=}CH_2;\quad HC{\equiv}CH$$

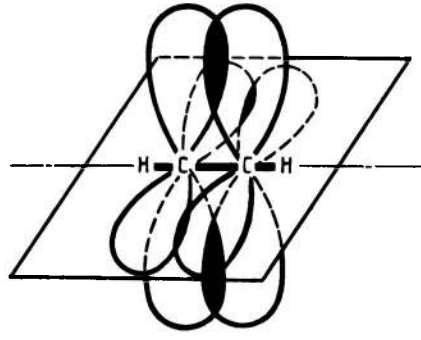


Fig. 39
Three-dimensional arrangement of the orbitals in an acetylene molecule

the carbon-carbon bond becomes shorter, the electronegativity of a carbon atom grows and, consequently, the C—H bond becomes more polar and reaches a maximum in the given series in acetylene.

The increase in the polarity of the C—H bond facilitates the appearance, for instance in acetylene, of weak acidic properties.

Physical Properties. The alkynes from C_2H_2 to C_4H_6 are gases under ordinary conditions, and from C_5H_8 to $C_{16}H_{30}$ are liquids. The same laws of the change in the boiling and melting points are observed as in the alkanes and alkenes.

Chemical Properties. Hydrogen is added in the presence of catalysts and includes the stage of formation of an intermediate alkene:

$$\underset{\text{Propyne}}{H_3C{-}C{\equiv}CH_3} \xrightarrow{+H_2} \underset{\text{Propene}}{H_3C{-}CH{=}CH_2} \xrightarrow{+H_2} \underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3}$$

Reactions with halogens follow a similar mechanism, except that two moles of a halogen are added. A vinyl cation forms in the intermediate step:

$$HC{\equiv}CH + Br^+ \rightarrow \underset{\text{Vinyl cation}}{\underset{\displaystyle Br}{\overset{|}{HC{=}C^+{-}H}}} \xrightarrow{+Br^-} \underset{\displaystyle Br}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{HC{=}CH}}}} \xrightarrow{+Br^-}$$

$$\rightarrow \underset{\displaystyle Br\ Br}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{HC{-}C^+{-}H}}}} \xrightarrow{+Br^-} \underset{\displaystyle Br\ Br}{\overset{\displaystyle Br\ Br}{\overset{|\ \ |}{\underset{|\ \ |}{H{-}C{-}C{-}H}}}}$$

Tribromoethyl cation — Tetrabromoethane

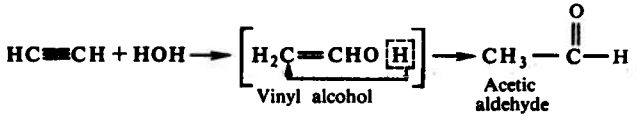
The reaction with hydrogen halides occurs in accordance with Markovnikov's rule:

$$H_3C{-}C{\equiv}CH + 2HCl \rightarrow H_3C{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}{-}CH_3$$

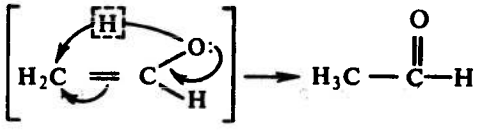
and produces dihalogen derivatives in which both halogens are bonded to one carbon atom.

Hydration. Water is added to alkynes in an acid medium in the presence of mercury(II) salts. Here acetylene yields acetaldehyde. This reaction was first described by the outstanding Russian chemist M. Kucherov in 1881.

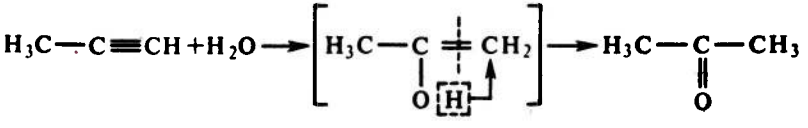
The intermediate—vinyl alcohol—is not stable and isomerizes to acetaldehyde:



Compounds in which an OH group is bonded to an aliphatic sp^2 hybridized carbon atom are called **enols.** The instability of such structures is explained by the mutual influence of the atoms:



Under the conditions of the Kucherov reaction, **ketones** form from alkynes:

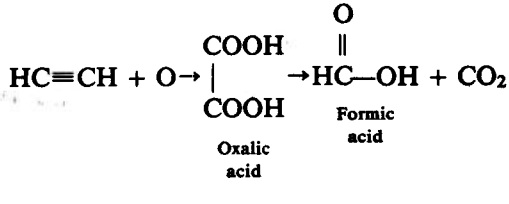


The Kucherov reaction is of a major industrial significance for the production of ethanol, acetaldehyde, acetic acid, etc.

Formation of Metallic Derivatives. These compounds form as a result of the substitution of the hydrogen atoms at an *sp* hybridized carbon atom, which is associated with acidic properties. For example, if acetylene is passed through an ammonia solution of silver nitrate (or CuCl), a precipitate of a metal acetylide forms:

$$HC{\equiv}CH + 2AgNO_3 + 2NH_4OH \rightarrow Ag{-}C{\equiv}C{-}Ag + 2NH_4NO_3 + 2H_2O$$
$$HC{\equiv}CH + 2CuCl + 2NH_4OH \rightarrow Cu{-}C{\equiv}C{-}Cu + 2NH_4Cl + 2H_2O$$

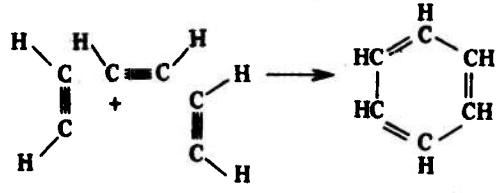
In the presence of potassium permanganate, acetylene readily oxidizes to oxalic acid, which, in turn, further decomposes into formic acid and carbon dioxide:



The polymerization of alkynes can proceed in several directions; for example, in linear polymerization, vinylacetylene mainly forms:

$$CH{\equiv}CH + CH{\equiv}CH \rightarrow \underset{\text{Vinylacetylene}}{CH_2{=}CH{-}C{\equiv}CH}$$

while in cyclic polymerization, benzene forms:



Benzene

Acetylene is a colourless gas. Pure acetylene has no odour. It burns with a bright smoking flame in the air:

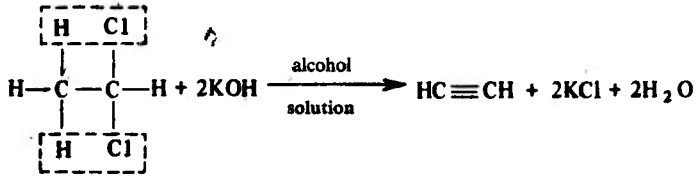
$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

A very high temperature (about 3000 °C) develops when acetylene is burned in a stream of oxygen. This is widely used for acetylene (oxyacetylene) welding.

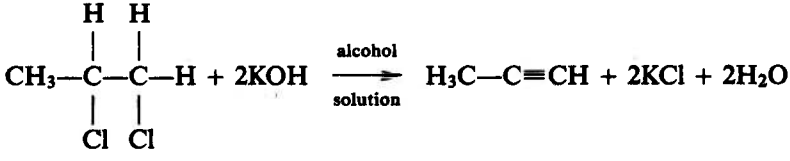
The most important applications of acetylene are the production of acetaldehyde, ethanol, acetic acid, and vinylacetylene. The latter is used in the synthesis of chloroprene rubber.

Production of Acetylene. We shall describe only three of the numerous methods of producing acetylene:

(1) from dihalogen derivatives containing the halogens at the same carbon atom. The reaction proceeds in an alcohol solution of an alkali:



(2) from dihalogen derivatives containing halogen atoms at two adjacent carbon atoms:



(3) from calcium carbide by reacting it with water:

$$Ca\begin{matrix}C\\ \|\\ C\end{matrix} + 2HOH \rightarrow Ca(OH)_2 + HC{\equiv}CH$$

Figure 40 shows examples of the industrial application of acetylene.

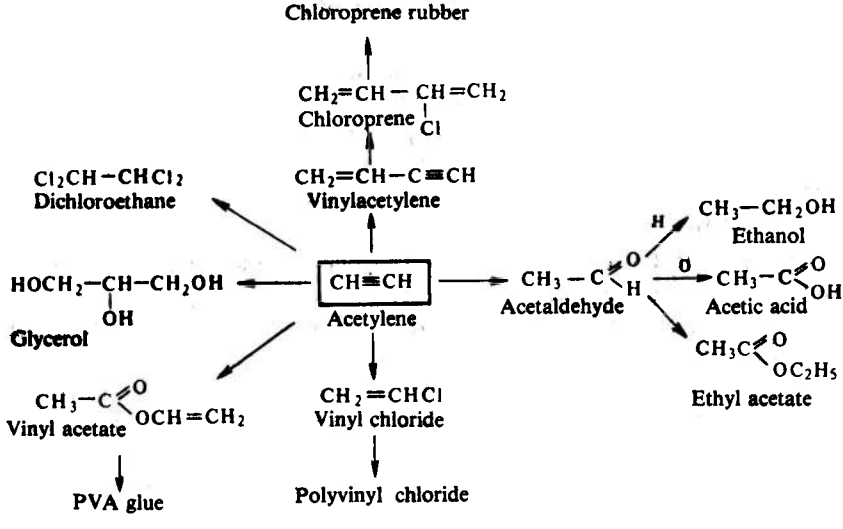


Fig. 40
The industrial applications of acetylene

Questions and Problems

1. Are *cis-trans* isomers possible for alkynes?
2. Write the equation of the Kucherov reaction and explain why the intermediate is not stable and isomerizes.
3. Write the reactions of polymerization of propene, propyne, and methylbutadiene.
4. For which of the following substances is geometric isomerization possible:

$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2;\quad CH_3{-}C{\equiv}C{-}CH_3;\quad CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_3;$$

$$CH_3{-}CH_2{-}CH{=}CH{-}CH_3$$

$$CH_3{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_3$$

5[a]. When 10 g of a calcium carbide specimen were treated with water, 2.24 lit of acetylene were obtained. What was the content of the CaC_2 in the specimen in per cent by mass?

6[a]. The acetylene produced from 200 g of calcium carbide containing 20% by mass of impurities was involved in a hydration reaction. What mass of acetaldehyde formed if the acetylene yield was 75% by mass of the theoretical one?

7*. At a laboratory, 8 g of benzene were obtained from 11.2 lit of acetylene. What was the yield of the benzene in per cent by mass of the theoretical one?

8*. The combustion of 1.3 g of a hydrocarbon yielded 4.4 g of CO_2 and 0.9 g of H_2O. The density of this substance relative to hydrogen was 13. Determine the formula of the hydrocarbon.

20.5. Aromatics. Benzene

The term "aromatic compounds" (later often abbreviated to "aromatics") applied at the beginning of the 19th century to benzene and its numerous derivatives is purely accidental in its origin. The first compounds of this series to be known (benzoic aldehyde, benzoic acid, toluene) were compounds having a pleasant odour. They were separated from aromatic balsams or other fragrant substances of a natural origin. The parent of the aromatics is benzene C_6H_6. In 1865, A. Kekulé first proposed a structure of benzene that explained its properties.

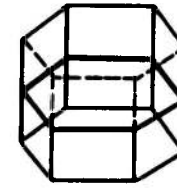
Structure of Benzene. Aromaticity. In a benzene molecule, all six carbon atoms are in the sp^2 hybridized state, are bonded to one another, and form a regular hexagon. The length of all the C—C bonds is the same and equals 0.140 nm. The internal bond angles are 120°. Each carbon atom is joined to two carbon and one hydrogen atoms by one *s* and two *p* electrons. The remaining *p* orbitals of the carbon atoms overlap uniformly and form a single *p* electron cloud. This occurs because the *p* orbital of each carbon atom is uniformly overlapped by the similar orbitals of two adjacent carbon atoms, which can be depicted as follows:



Overlap of $2p$ atomic orbitals in benzene molecule. "Top view"

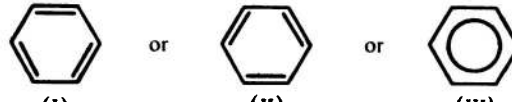


"Side view"



Formation of single pi electron system in benzene. "Side view"

Unlike alkenes, in benzene the electrons of the pi bonds are not confined in the spaces between each pair of carbon atoms, but are uniformly distributed between all six atoms, i.e. they are **delocalized.** The single pi electron cloud is above and below the plane of the six-membered ring (Fig. 41). Hence, the structure of benzene can be depicted as follows:



(I) or (II) or (III)

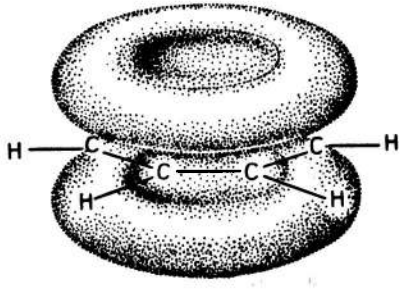


Fig. 41
A benzene molecule:
The pi cloud is above and below the ring plane

Structure (III) reflects the main feature—the uniformity of pi electron distribution between the carbon atoms—most satisfactorily. But structures (I) and (II) (the Kekulé structures) are still widely used because they are convenient to write and explain reaction mechanisms.

Benzene differs from the hydrocarbons considered previously in features known collectively as **aromatic properties.** *The length of the C—C bonds in benzene is near the mean value of a single bond* (0.154 nm) *and an ethylene double bond* (0.134 nm). *The carbon atoms form a regular plane hexagon in which the electron density is uniformly distributed between all the carbon atoms.* Instead of conventional double bonds, benzene has a single delocalized pi electron cloud.

Hence, the name aromatics is applied to compounds whose molecules have a plane cyclic structure containing a closed delocalized pi electron cloud. The six pi electrons in benzene are called its aromatic sextet.

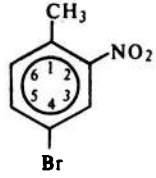
Nomenclature and Isomerism. The first homologue of benzene—methylbenzene or toluene, has no isomers. The next member of this series—C_8H_{10}—can have several isomers: ethylbenzene, and also three dimethylbenzenes—*ortho-*, *meta-*, and *para*-xylenes:



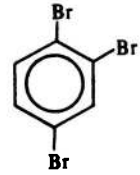
Methylbenzene (toluene) | Ethylbenzene | *ortho*-Xylene | *meta*-Xylene | *para*-Xylene

Dimethylbenzenes

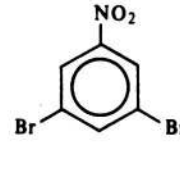
The relevant IUPAC names for the dimethylbenzenes are 1,2-dimethylbenzene, 1,3-dimethylbenzene, and 1,4-dimethylbenzene. Numbers are also used if there are more than two substituents in benzene, having in view that here the lowest possible numbers must be obtained:



2-Nitro-
4-bromotoluene



1,2,4-Tri-
bromobenzene



3,5-Dibromo-
nitrobenzene

Physical Properties. The lower members of the homologous series of benzene under ordinary conditions are colourless liquids with a typical odour (Table 8). They do not mix with water, but mix readily with non-polar organic solvents. The boiling points of isomers do not differ greatly: *ortho-* (2-) isomers generally boil at a higher temperature than *para-* (4-) ones.

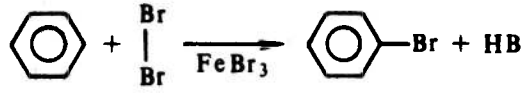
Table 8

Selected Members of the Aromatics

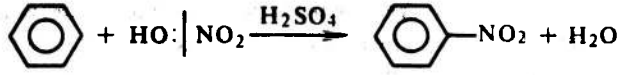
Name		M.p., °C	B.p., °C
Trivial	IUPAC		
Benzene	Benzene	5	80
Toluene	Methylbenzene	−93	111
ortho-Xylene	1,2-Dimethylbenzene	−28	144
meta-Xylene	1,3-Dimethylbenzene	−53	139
para-Xylene	1,4-Dimethylbenzene	+13	138
Ethylbenzene	Ethylbenzene	−95	136

Chemical Properties. The pi-electron system of benzene is susceptible to an attack by electrophilic reagents and to a certain extent screens from an attack by nucleophiles. *The most typical of benzene is a reaction of electrophilic substitution* (S_E). Examples of the latter are halogenation and nitration.

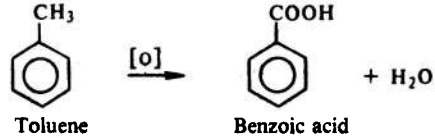
Halogenation. The reaction proceeds in the presence of catalysts whose role consists in polarization of a halogen molecule with the subsequent formation of an electrophilic particle:



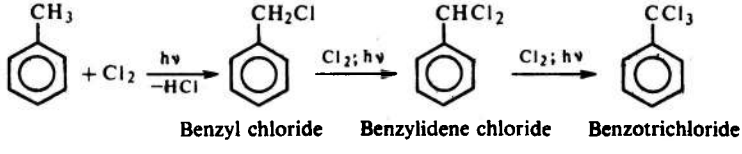
Nitration. A nitronium cation $[NO_2]^+$ is the electrophilic particle in this reaction:



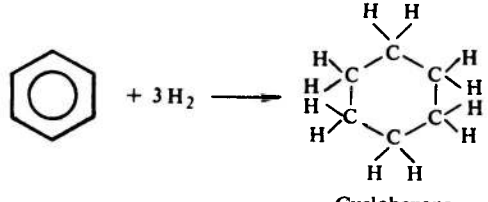
Benzene exhibits a high stability to oxidizing agents, but its homologues are oxidized much more readily. For example, when an aqueous solution of $KMnO_4$ is reacted with toluene, the latter is oxidized to benzoic acid:



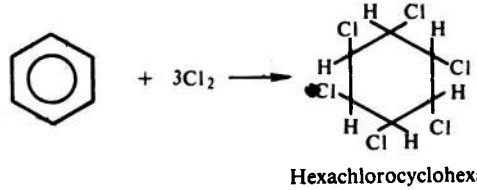
Benzene homologues (e.g., toluene) can enter into radical substitution reactions, but here the substitution occurs in a side chain, i.e. in the alkyl radical. The hydrogen atoms are substituted by chlorine in the light when heated (in the gas phase) by an S_R mechanism:



Addition Reaction. This type of reactions with benzene and its homologues proceeds with great difficulty and generally under rigorous conditions. For instance, hydrogen is added to benzene in the presence of catalysts and at high temperatures:



Chlorine is added in ultraviolet light. Depending on the conditions, benzene can add up to six chlorine atoms:

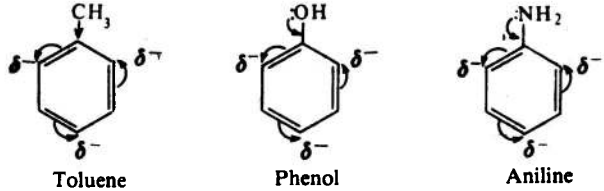


Rules of Orientation in the Benzene Ring. In the above reactions of halogenation and nitration (S_E reactions), the attacking particle reacts with the unsubstituted benzene and therefore the product—monosubstituted benzene—has no isomers. But if the benzene ring has a substituent, the remaining five carbon atoms become unequivalent. With respect to the substituent, two *ortho-* (2-), two *meta-* (3-), and one *para-* (4-) positions are distinguished. This is why the position of a second entering substituent will depend on two very important factors, namely, the nature of the first substituent and the nature of the attacking reagent.

The substituent already on a benzene ring has an orienting effect on a second substituent and directs it to a strictly definite position.

Two groups of substituents are distinguished depending on their orienting effect. The first one includes *ortho-* and *para*-directors, and the second—*meta*-directors.

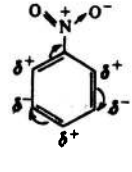
The *o-* and *p*-directors are electron donors in their nature and increase the electron density of the benzene ring by supplying it with electrons. This, in turn, causes the redistribution of the electron density in the ring which creates a surplus of electrons in the *ortho-* and *para*-positions. The *o-* and *p*-directors include alkyl radicals (—CH_3, —C_2H_5, etc.), and also —OH, —NH_2, and so on. The shift of the electron density of the benzene ring in toluene, phenol, and aniline is shown below:



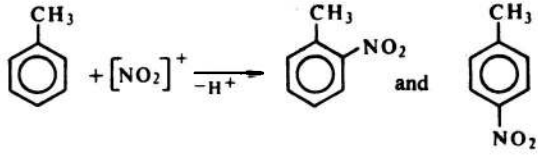
Toluene Phenol Aniline

In phenol and aniline, the unshared pairs of electrons of the oxygen and nitrogen interact respectively with the pi electrons of the benzene ring. The symbol $\delta-$ shows the positions at which the electron density grows.

Meta-directors (—N=O, NO_2, —COOH, —C(=O)—H, etc.), being electron acceptors, pull back the electron cloud from the benzene ring in their direction. As a result, the electron density in the benzene ring lowers somewhat, especially in the *ortho-* and *para*-positions:

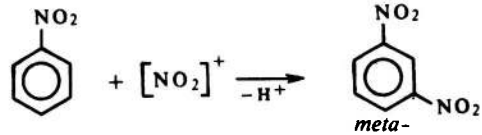


The nature of the attacking reagent substantially affects the structure of the product. If a benzene ring contains an *o*- or *p*-director, then *ortho*- or *para*-isomers will form in S_E reactions:



ortho-Nitrotoluene *para*-Nitrotoluene

If a benzene ring contains an *m*-director, a *meta*-isomer will form in an S_E reaction:



Nitrobenzene *meta*-Dinitrobenzene

Representatives of the Aromatics. Benzene C_6H_6 is a colourless transparent liquid with a typical odour boiling at 80.1 °C. It mixes poorly with water and dissolves well in ether. It is used as a solvent. In the industry, it is the starting material for producing phenols, styrene, aniline, explosives, etc. It is poisonous and an explosion hazard. The radical $—C_6H_5$ is called **phenyl.**

Toluene $C_6H_5—CH_3$ (methylbenzene) is a colourless liquid with a typical odour boiling at 110 °C. It is insoluble in water. It mixes with benzene and ether in all proportions. It is widely used to produce benzoic acid C_6H_5COOH, explosives (nitrotoluenes), dyes, etc.

Styrene $C_6H_5CH=CH_2$ is a liquid with a pleasant odour. It readily polymerizes, which is widely used in the production of polystyrene. In combination with butadiene, it is employed in the production of polystyrene rubber.

Questions and Problems

1. Disclose the essence of the concepts: aromaticity, aromatic sextet, benzene ring, delocalization of pi bonds, the orientation rules in a benzene ring, *ortho*-, *para*-, and *meta*-substituents.

2. Explain the causes of pi electron delocalization in benzene.

3. While benzene seems to be unsaturated, it readily enters into displacement reactions, whereas alkenes and alkynes, conversely, readily enter into addition reactions. What is the reason for such an apparent anomaly of benzene?

4. Explain the structure of a carbocation and carbanion using any hydrocarbons as an example.

5. Indicate specific examples of electrophilic and nucleophilic particles and explain their structure.

6. What does the symbol S_R signify? Give an example of a reaction proceeding by this mechanism.

7. What is the difference between the mechanisms of reactions S_E and S_N? Give examples of specific reactions.

8. Explain the mechanisms of the homolytic and heterolytic cleavage of a covalent bond using hydrocarbons as examples.

9. Describe the structure of a methyl radical.

10. Show how methane, ethylene, and acetylene relate to bromine, water, and hydrogen.

11. Why is a polymerization reaction impossible for aromatics?

12. How do the main tenets of Butlerov's structural theory manifest themselves in hydrocarbons?

13. How are organic reactions classified? Use examples of hydrocarbons to show each type of reaction.

14[a]. The bromination of 15.6 g of benzene yielded 20 g of bromobenzene. What was the yield of the bromobenzene in per cent by mass of the theoretical value?

15[a]. Symmetrical trimethylbenzene (1,3,5-trimethylbenzene) can be prepared from an acetylene homologue. Write the equation of the reaction and calculate the volume of the homologue needed to obtain 48 g of trimethylbenzene.

SUMMARY

Hydrocarbons are organic compounds consisting only of carbon and hydrogen. Saturated, unsaturated, and aromatic hydrocarbons are distinguished. In the saturated hydrocarbons, the carbon atoms are in the sp^3 hybridized state. Alkenes have two sp^2 hybridized carbon atoms between which a pi bond forms in addition to the sigma bond as a result of the overlap of their p orbitals. Alkynes have two sp hybridized carbon atoms joined by one sigma and two pi bonds. The transition from methane to acetylene is attended by a change in the geometry of the molecules, which is determined by the state of hybridization of the carbon atom.

A special place is occupied by the aromatics, whose parent is benzene. A distinguishing feature of benzene is its plane cyclic structure with a single pi electron system. All the carbon atoms in benzene are equivalent, which is explained by the delocalization of the pi electrons.

Alkanes mainly enter into reactions of radical substitution (S_R) while alkenes and alkynes enter into addition reactions. Alkenes and alkynes react with water, hydrogen halides, and other polar molecules in accordance with Markovnikov's rule. This rule shows the essence of the mutual influence of atoms in molecules.

Dienes react with halogens and hydrogen halides to form chiefly addition products at positions 1 and 4. This is explained by the structure of the intermediately formed carbocation.

Aromatics can readily enter into electrophilic substitution reactions. The nature of the product is determined by the orientation rules and the nature of the attacking reagent.

CHAPTER 21

HYDROXY DERIVATIVES OF HYDROCARBONS

OBJECTIVES

To be able to distinguish alcohols from phenols and explain the concept of atomicity; to know the electron structure of alcohols, phenols, and their common properties; to be able to distinguish the properties of phenol hydroxyl from alcohol hydroxyl; to know the properties of polyatomic alcohols and their difference from monatomic ones.

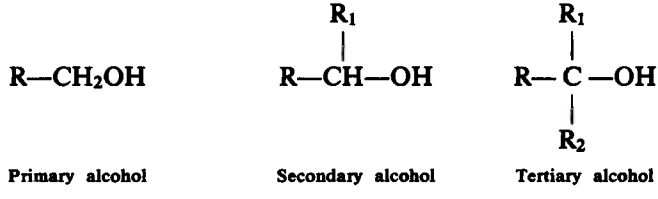
21.1. Saturated Monatomic Alcohols

Depending on the nature of the hydrocarbon radical, the hydroxy derivatives of hydrocarbons are divided into **alcohols** and **phenols.**

If a hydroxyl group is bonded directly to an aromatic (benzene) ring, such derivatives are called phenols, while the hydroxy derivatives of the other hydrocarbons (aliphatic and alicyclic series) are called alcohols.

The number of hydroxyl groups determines the atomicity of alcohols and phenols, hence we distinguish monatomic, diatomic, triatomic, etc. alcohols and phenols.

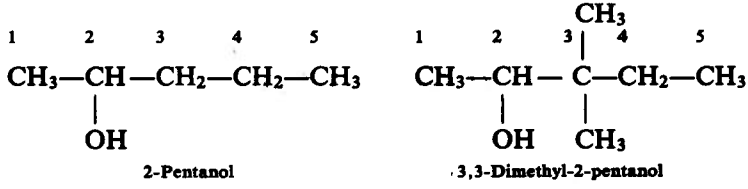
The representatives of the monatomic alcohols correspond to the general formula $C_nH_{2n+1}OH$. The hydroxyl group can be bonded to a primary, secondary, or tertiary carbon atom, the compound formed being a **primary, secondary,** or **tertiary** alcohol, respectively:



Nomenclature and Isomerism. By the IUPAC nomenclature, the name of an alcohol is formed from the name of the relevant hydrocarbon with replacement of the *–e* ending by *–ol* for monatomic alcohols. For diatomic ones, the suffix *–diol* is added to the name of the hydrocarbon, and so on.

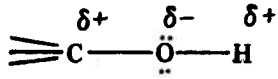
By this system, alcohols are named as derivatives of the longest carbon chain containing the —OH group. The chain of carbon atoms is numbered

from the end that gives the carbon containing the —OH group the lowest number:



Hence, isomerism in the alcohol series depends both on the isomerism of the chain of carbon atoms and on the position of the hydroxyl group.

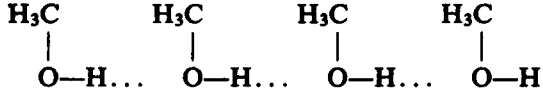
Structure of Alcohols. The features of alcohols are determined primarily by the presence of the functional group —OH. In an alcohol molecule, the group of atoms



is polarized because the electronegative oxygen pulls back the electrons from both the hydrogen atom and the hydrocarbon radical. Consequently, such polarization can facilitate cleavage of the bonds on the sections O—H, C—O, or O—H and C—O simultaneously. The latter type of bond breaking is oxidation of alcohols. The structural features of alcohols determine their acid-base properties.

Physical Properties. Alcohols are colourless (in a thin layer) neutral compounds; the lower members of the homologous series have a burning taste. The solubility of alcohols in water diminishes with an increase in their molecular mass. Methanol, ethanol, and propanol mix with water in any proportions, whereas the following members of the homologous series (butanol, the pentanols) have a limited solubility in water.

The higher alcohols are insoluble in water. Alcohols, like water, are associated high-boiling liquids (Table 9), which is due to the presence of hydrogen bonds:



Chemical Properties. Reactions with the participation of alcohols can be divided into three groups:

(1) substitution of the hydrogen in the hydroxyl group;

(2) reactions proceeding with the participation of the hydroxyl group itself;

(3) processes in which a hydroxyl group and a hydrocarbon radical are involved simultaneously.

Table 9

Physical Properties of Selected Monatomic Alcohols

Name		Formula	T_m, °C	T_b, °C
Trivial	IUPAC			
Methyl alcohol	Methanol	CH_3OH	−98	+65
Ethyl alcohol	Ethanol	$CH_3—CH_2OH$	−114	+78
Propyl alcohol	1-Propanol	$CH_3—CH_2—CH_2OH$	−127	+97
Isopropyl alcohol	2-Propanol	$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$	−89	+82
Primary butyl alcohol	1-Butanol	$CH_3—CH_2—CH_2—CH_2OH$	−80	+117

1. The polarity of the O—H bond facilitates the elimination of hydrogen in the form of an ion. The remaining anion (an alkoxy anion $CH_3O:^-$, $C_2H_5O:^-$, etc.) has nucleophilic properties. This feature of alcohols determines their acid properties, which is indicated by the reactions of substitution of the hydroxyl hydrogen by an active metal. The products are called **alcoholates:**

$$2CH_3—CH_2—OH + 2Na \rightarrow \underset{\text{Sodium ethylate}}{2CH_3—CH_2—ONa} + H_2$$

Alcoholates are unstable compounds and in the presence of traces of water they readily hydrolyze with the formation of a metal hydroxide and the relevant alcohol:

$$CH_3—CH_2—ONa + HOH \rightarrow CH_3—CH_2—OH + NaOH$$

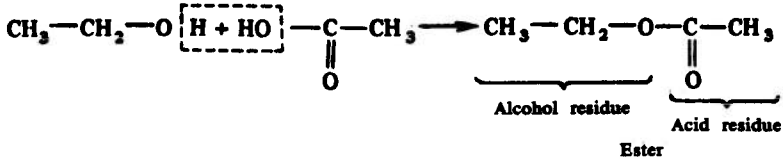
In the presence of dehydrating catalysts, alcohols can react with one another to form ethers:

$$C_2H_5O\boxed{H + HO}C_2H_5 \xrightarrow[-H_2O]{H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5}$$

Ethers can be considered as a product of substitution of the hydroxyl group hydrogen by a hydrocarbon radical, which can be illustrated by the following reaction:

$$\underset{\text{Sodium ethylene}}{C_2H_5ONa} + \underset{\text{Ethyl iodide}}{I—C_2H_5} \rightarrow \underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + NaI$$

The same group of reactions includes the reaction of alcohols with organic acids with the formation of an ester:



2. The ability of the oxygen's unshared pair of electrons to attach a proton and form an oxonium cation explains the properties of alcohols as bases:



When alcohols are reacted with hydrogen halides, the hydroxyl group is substituted by a halogen:

$$C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$$

The reaction of an alcohol with a hydrogen halide is reversible: water shifts equilibrium to the left, while the addition of an alkali facilitates complete hydrolysis. On the other hand, in the presence of a dry hydrogen halide (in a non-aqueous medium), equilibrium shifts to the right:

$$C_2H_5Br \underset{HBr}{\overset{HOH}{\rightleftarrows}} C_2H_5OH$$

When an alcohol, e.g. ethanol, reacts with concentrated sulphuric acid, alkyl sulphates form:

$$CH_3—CH_2—OH + HO—SO_3H \xrightarrow[-H_2O]{100°C} \underset{\substack{\text{Ethyl sulphate}\\ \text{(Ethyl sulphuric}\\ \text{acid)}}}{C_2H_5—OSO_3H}$$

that can be used to produce compounds of various classes. For instance, if ethyl sulphuric acid is heated in the presence of an excess of sulphuric acid to 170 °C, it decomposes into ethylene and water. Consequently, in the presence of concentrated sulphuric acid and with heating, alcohols experience **intramolecular dehydration:**

$$\begin{array}{l} H_2C—CH_2 \xrightarrow{H_2SO_4} H_2C=CH_2 + H_2O \\ \quad\;| \quad\; | \qquad\qquad\quad \text{Ethylene} \\ \quad H \quad OH \end{array}$$

If ethyl sulphuric acid is heated in the presence of an alcohol, an ether forms:

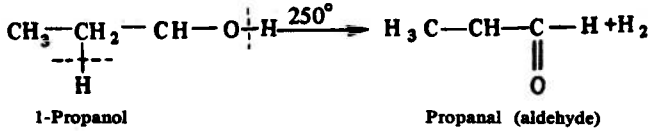
$$C_2H_5—OSO_3H + C_2H_5OH \rightarrow H_5C_2—O—C_2H_5 + H_2SO_4$$

On the other hand, the addition to ethyl sulphuric acid of acetic acid (or any other carboxylic acid) yields **esters:**

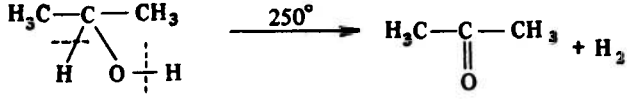
$$C_2H_5OSO_3H + HO-\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2SO_4$$

3. The polarity of the bond $\rangle C-O$ promotes heterolytic bond breaking, owing to which the OH group detaches in the form of an anion.

When alcohol vapour is passed over copper, hydrogen is eliminated (dehydrogenation), and **oxo compounds** form, namely, *primary alcohols yield aldehydes, and secondary ones—ketones:*

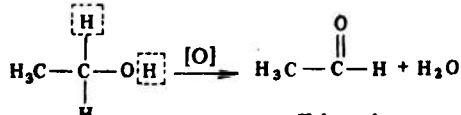


1-Propanol — Propanal (aldehyde)

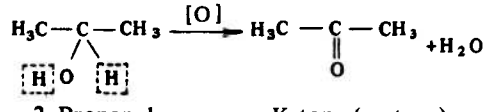


2-Propanol — Propanone (ketone)

Oxidizing agents cause the simultaneous breaking of the O—H bonds and C—H bonds at the carbon atom joined to the hydroxyl group. *Primary alcohols are oxidized to aldehydes, and secondary ones to ketones:*



Ethanol — Ethanal (acetaldehyde)



2-Propanol — Ketone (acetone)

Production of Monatomic Alcohols. Of the numerous methods of producing alcohols, we shall note only the ones having an industrial significance:

(a) the reduction of aldehydes and ketones yields primary and secondary alcohols, respectively. For example, ethanol is produced from acetaldehyde:

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{[H]} C_2H_5OH$$

(b) the hydration of alkenes in the presence of catalysts:

$$CH_2 = CH_2 + HOH \rightarrow \underset{\text{Ethanol}}{C_2H_5OH}$$

(c) the fermentation of saccharous substances:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{enzyme}]{} 2C_2H_5OH + 2CO_2\uparrow$$

Representatives of Monatomic Alcohols. Methanol (methyl or wood alcohol) is a colourless transparent liquid with a typical odour. *It is poisonous!* It is obtained by the dry distillation of wood, and also from carbon monoxide and hydrogen:

$$CO + H_2 \rightarrow CH_3OH$$

Ethanol (ethyl alcohol) is a colourless transparent liquid with a typical odour. It mixes with water in any proportions. Ethanol is produced commercially by the hydration of ethylene or the reduction of acetaldehyde formed from acetylene in Kucherov's reaction.

Ethanol is widely used in industrial organic synthesis to produce rubber, chloroform, diethyl ether, and so on, as well as a solvent.

Questions and Problems

1. Compare the properties of monatomic alcohols with those of saturated hydrocarbons and explain why they are different.

2. How can the following transformations be carried out:

(a) $CH_3-CH_3 \rightarrow CH_2=CH_2 \rightarrow C_2H_5OH$; $CH_3-CH_3 \rightarrow CH_3-CH_2I \rightarrow C_2H_5OH$

(b) $CH_4 \rightarrow HC\equiv CH \rightarrow H_2C=CH_2 \rightarrow CH_3-CH_2I \rightarrow C_2H_5OH \rightarrow C_2H_5O-\overset{\overset{O}{\|}}{C}-CH_3$

3. Why is 1-propanol called a primary alcohol, and 2-propanol, a secondary one?

4. Write all the possible isomers of the compound $C_6H_{13}OH$ and name them by the IUPAC nomenclature.

5. Write the reaction of obtaining diethyl ether from acetylene.

6. Propene was treated with hydrogen iodide, and the product was reacted with an aqueous solution of an alkali. The formed substance (what?) was separated and then heated in the presence of sulphuric acid. Describe the relevant reactions.

7*. What volume of hydrogen evolves when 1.15 g of sodium are reacted with ethanol?

8*. Calculate the masses of ethanol and metallic sodium needed to obtain 1.12 lit of hydrogen.

9*. When 1.85 g of a monatomic alcohol were reacted with metallic sodium, 0.28 lit of hydrogen evolved. Determine the relative molecular mass and structural formula of the alcohol having in view that it is a primary one.

10*. When 1.5 g of an alcohol were reacted with concentrated sulphuric acid, 0.56 lit of an alkene was obtained. Name the initial alcohol. Defend your answer with calculations.

11*. What was the yield of diethyl ether in per cent by mass of the theoretical value if 18.5 g of the ether were obtained from 46 g of ethanol?

12*. In 100 g of ethanol there were dissolved 2.3 g of metallic sodium. What was the mass of the obtained solution? Determine the per cent concentration by mass of the sodium ethylate in the solution.

21.2. Ethylene Glycol and Glycerol

Ethylene glycol $\begin{matrix}CH_2—CH_2\\ |\quad\quad |\\ OH\quad OH\end{matrix}$ is the first representative in the homologous series of diatomic alcohols. Diatomic alcohols, or glycols, by the IUPAC nomenclature are called **diols.** For instance, ethylene glycol by this nomenclature is ethanediol.

Ethylene glycol is produced commercially from ethylene:

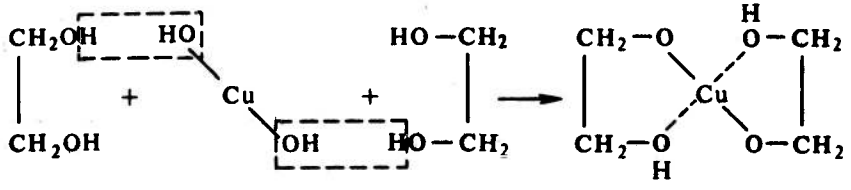
$$CH_2=CH_2 \xrightarrow{+Cl_2} \begin{matrix}CH_2—CH_2\\ |\quad\quad |\\ Cl\quad\quad Cl\end{matrix} \xrightarrow[-2HCl]{+2HOH} \begin{matrix}CH_2—CH_2\\ |\quad\quad |\\ OH\quad\quad OH\end{matrix}$$

1,2-Dichloroethane

Ethylene glycol is a thick colourless liquid boiling at 197 °C. It has a sweet taste. It mixes with water in any proportions. *It is poisonous!*

The chemical properties of diatomic alcohols (glycols) are similar to those of monatomic ones. All the reactions that were described for monatomic alcohols are also typical of diatomic ones. They can enter into a reaction at the expense of either one or both hydroxyl groups.

An increase in the number of hydroxyl groups in alcohols is attended by a growth in their acidic properties. Therefore, unlike monatomic alcohols, glycols react with copper(II) hydroxide to form the complex copper glycolate:



Ethylene glycol is widely used as an antifreeze, and in the production of plasticizers (softeners) used in the paint and varnish industry.

Glycerol $CH_2(OH)-CH(OH)-CH_2(OH)$ is a representative of the triatomic alcohols.

Its IUPAC name is **1,2,3-propanetriol.** Glycerol is a colourless transparent viscous liquid with a sweet taste. It is hygroscopic. It mixes with water in any proportions.

The chemical activity of glycerol is higher than that of monatomic alcohols. One, two, or all three hydroxyl groups can participate in reactions. For example, in a reaction with hydrogen halides they can be substituted consecutively and form a trihalogen derivative in the long run:

$$CH_2(OH)-CH(OH)-CH_2(OH) \xrightarrow[-H_2O]{+HCl} CH_2(Cl)-CH(OH)-CH_2(OH) \xrightarrow[-H_2O]{+HCl}$$

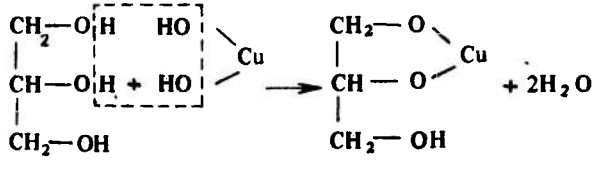
Glyceryl monochloride

$$\rightarrow CH_2(Cl)-CH(Cl)-CH_2(OH) \xrightarrow[-H_2O]{+HCl} CH_2(Cl)-CH(Cl)-CH_2(Cl)$$

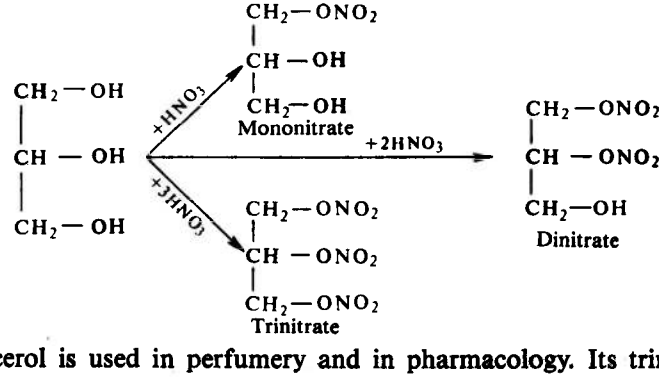
Glyceryl dichloride

Glyceryl trichloride (1,2,3-trichloropropane)

Glycerol reacts with the hydroxides of some metals including copper(II) to form glycerates. This reaction is used to identify polyatomic alcohols:



Copper glycerate has a typical blue colour. When glycerol reacts with nitric acid, mono-, di-, and trinitrates form depending on the amount of the acid used:



Glycerol is used in perfumery and in pharmacology. Its trinitrate in small doses can dilate the cardiac vessels, which is widely used in medicine.

Questions and Problems

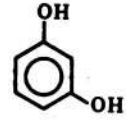
1. How does the mutual influence of the hydroxyl groups express itself in polyatomic alcohols?
2. What is the difference between a tertiary and a triatomic alcohol?
3. Can glycerol nitrates be considered as esters?
4. Why do polyatomic alcohols, unlike monatomic ones, react with copper(II) hydroxide?

21.3. Phenols

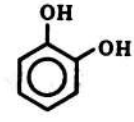
The parent of this class of compounds is the simplest phenol C_6H_5OH. Three isomers of diatomic phenols are known:



Hydroxyquinone (1,4-dihydroxybenzene)



Resorcinol (1,3-dihydroxybenzene)



Catechol (1,2-dihydroxybenzene)

Structure of Phenol. The pi electron system of the benzene ring partly overlaps with the *p* orbital of the oxygen atom containing an unshared electron pair. As a result, a common pi system forms whose density shifts in the direction of the benzene ring:



Hence, the hydroxyl group, by increasing the electron density in the *ortho*- (2-) and *para*- (4-) positions, facilitates reactions of electrophilic substitution in the benzene ring.

The benzene ring, in turn, appreciably affects the mobility of the hydroxyl group hydrogen. Shifting of the electrons along the C—O bond leads to considerable polarization of the O—H bond, hence the hydrogen is eliminated as an ion, i.e. dissociation is possible. Phenols are much stronger acids than alcohols, although as a whole they are much weaker than mineral acids.

Physical Properties. Phenol, or carbolic acid, is a colourless crystalline substance with a typical odour. It dissolves in water in the proportion 1:15.

The crystal hydrate $C_6H_5OH \cdot H_2O$ melts at 16 °C. It dissolves well in organic solvents. Phenol crystals turn pink in the air owing to oxidation. ***Phenol is poisonous.*** It causes burns when it gets on the skin.

Chemical Properties. Reactions with the participation of phenols can be divided into two groups—relative to the hydroxyl group and to the aromatic ring. The hydroxyl group reacts with alcohols, acids, oxides, hydroxides, and alkyl halides. The aromatic ring mainly participates in electrophilic substitution reactions according to the orientation rules.

The acid properties of phenol manifest themselves in reactions with bases. The formed phenolates, unlike alcoholates, can exist in aqueous solutions of alkalies:

$$C_6H_5OH \rightleftarrows \underset{\text{Phenolate ion}}{C_6H_5O^-} + H^+$$

$$C_6H_5OH + NaOH \rightarrow \underset{\text{Sodium phenolate}}{C_6H_5ONa} + H_2O$$

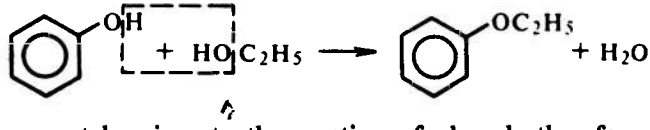
Phenolates (like alcoholates) can be obtained when phenols react with metals:

$$2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$$

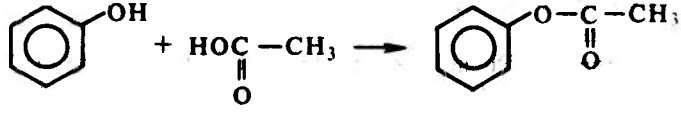
Since phenol is a weak acid, it can be displaced from phenolates by carbon dioxide:

$$C_6H_5ONa + CO_2 + H_2O \rightarrow C_6H_5OH + NaHCO_3$$

Phenols react with alcohols to form ethers:

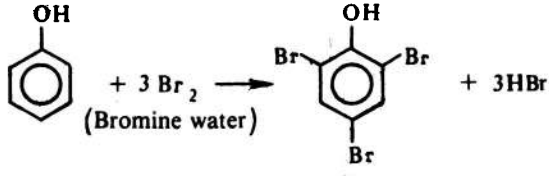


Attention must be given to the reaction of phenol ether formation: the water separates at the expense of the hydroxyl group of the alcohol and the hydrogen of the phenol hydroxyl. This indicates that the C—O bond in phenols is much stronger than in alcohols because of the interaction of the benzene ring pi electrons with the unshared pair of oxygen electrons. This is why *the* OH *group in phenols is not substituted by other atoms or groups of atoms as in alcohols.* The reaction of a phenol with a carboxylic acid yields an ester:



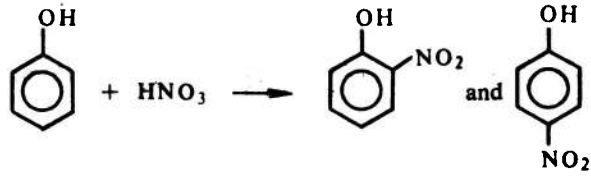
Electrophilic substitution reactions (bromination, nitration) proceed much more readily than in benzene.

For example, a reaction of phenol with bromine water yields tribromphenol. This reaction is often used for the qualitative and quantitative determination of phenol:



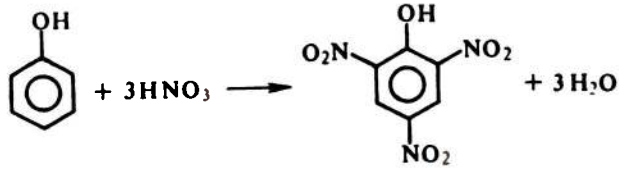
Tribromphenol

The reaction of phenol with dilute nitric acid yields a mixture of 2- and 4-nitrophenols:

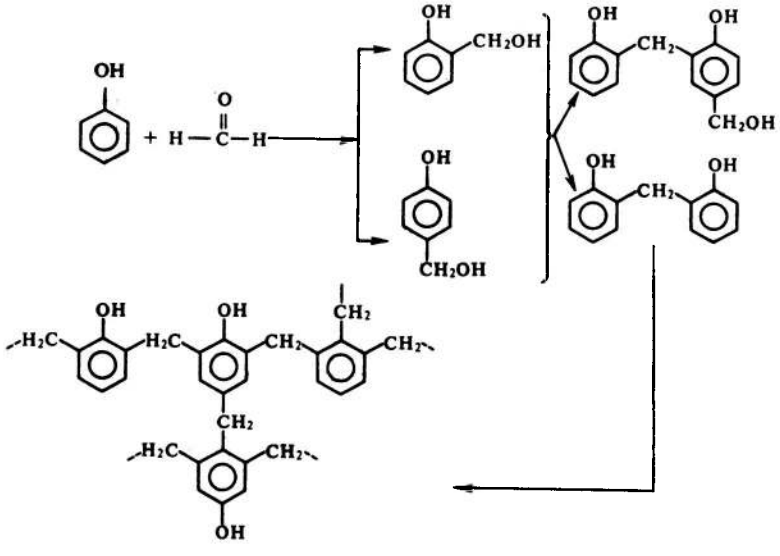


2-Nitrophenol 4-Nitrophenol

Nitration with nitric acid of a moderate concentration makes it possible to obtain 2, 4,6-trinitrophenol:



Phenol enters into a reaction of polycondensation with formaldehyde to form resinous products. These compounds are called phenolformaldehyde resins. In these reactions, there is first formed a mixture of 2- and 4-derivatives containing hydroxymethyl groups —CH_2OH in these positions relative to the phenol hydroxyl group. These compounds next again condense and in the long run form three-dimensional network structures:



Phenolic plastics are widely used in engineering in addition to other plastics.

Phenol is used in large amounts in the production of dyes, drugs, explosives, etc. A dilute solution of phenol in water (a 3% solution) is employed externally as an effective disinfectant.

Questions and Problems

1. Why do alcohols react with hydrogen bromide, while phenols do not?
2. Phenols do not have basic properties, while alcohols do. Explain these features.
3. Using phenol as an example, explain the mechanism of the nitration reaction and the reason why 2-nitrophenol forms.
4. Write the structural formula of *meta*-cresol (3-methyl phenol). Proceeding from this structure, indicate the possible halogenation products if the process is conducted (a) at a high temperature and in the light, and (b) in the cold in the presence of $FeBr_3$.

5[a]. The nitration of 2.3 g of phenol yielded 2.3 g of trinitrophenol. What was the yield of the trinitrophenol in per cent by mass of the theoretical value?

6[a]. To neutralize 100 g of a phenol solution, 0.5 g of sodium hydroxide was used. What was the per cent concentration by mass of the phenol in the initial solution?

7[a]. When 100 g of a solution of ethanol and phenol in benzene were reacted with metallic sodium, 1.12 lit of hydrogen evolved. When the same volume of the solution was reacted with bromine water, 16.55 g of a tribromo derivative were obtained. Calculate the per cent concentrations by mass of the ethanol and phenol in the solution.

8[a]. What mass of bromine is needed to convert 1 g of phenol into tribromphenol?

SUMMARY

The hydroxyl derivatives of hydrocarbons are alcohols and phenols. The latter differ from the alcohols in that the OH group in them is directly joined to an aromatic (benzene) ring.

The presence of electronegative oxygen leads to the considerable mobility of the hydroxyl group hydrogen. The nature of a hydrocarbon radical substantially affects the stability of the —C—O— and O—H bonds. In phenols, the unshared pair of oxygen electrons (*p* electrons) interact with the pi system of the benzene ring, owing to which a single pi electron cloud forms. This interaction explains the much higher stability of the —C—O— bond in phenols in comparison with alcohols. Phenols do not react with hydrogen halides, and the hydroxyl group is not substituted by other groups. Conversely, in alcohols, the hydroxyl group is substituted by halogen when they react with hydrogen halides.

The nature of the radical also noticeably affects the acidic properties, namely, phenols are much stronger acids than alcohols. The basic properties of alcohols are determined by their ability of protonation with the formation of an alkyloxonium ion. Phenols do not have basic properties.

The hydroxyl group in phenols substantially affects the reactivity of the benzene ring. Being an electron donor, it can increase the electron density in the ring and thus promote electrophilic substitution reactions. Nitration, and halogenation of phenol occur chiefly in the 2- (*ortho*-) and 4- (*para*-) positions.

CHAPTER 22

ALDEHYDES AND KETONES

OBJECTIVES

To know the structural difference of aldehydes from ketones; the electron structure of the carbonyl group; to see how hydrocarbon radicals affect the reactivity of aldehydes and ketones; to know the mechanism of the reaction of nucleophilic addition; to know reactions for distinguishing aldehydes from ketones.

22.1. Structure of the Carbonyl Group

The **carbonyl group** $>C=O$ is the structural unit determining virtually all the properties of aldehydes and ketones. In aldehydes, it is bonded only to one hydrocarbon radical and one hydrogen atom (the radical may also

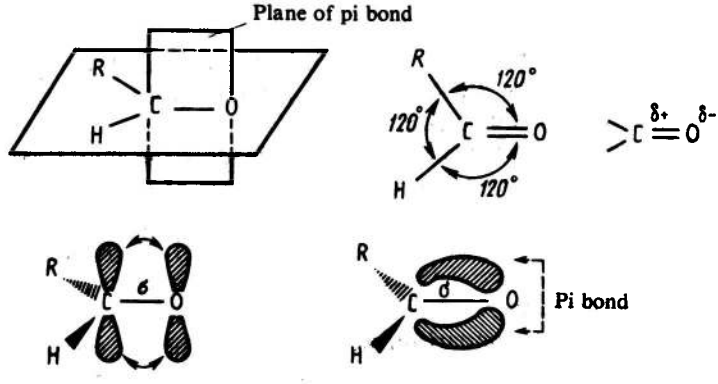
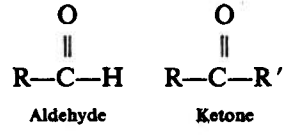


Fig. 42
Structure of a carbonyl group

be hydrogen), whereas in ketones it is bonded to two radicals (excluding hydrogen):

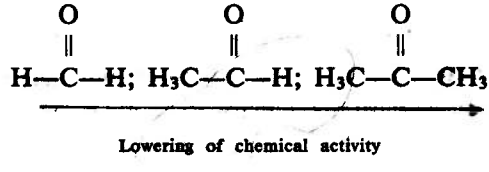


(the radicals R and R′ may be identical).

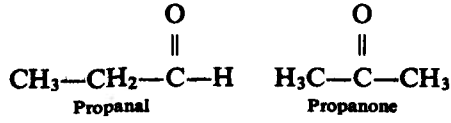
The carbon atom in the carbonyl group is in the sp^2 hybridized state and is joined to one oxygen atom by a double bond (one sigma bond and one pi bond) that in its physical nature is similar to a carbon-carbon double bond.

A feature of the carbonyl group is the fact that the pi electron cloud is shifted toward the more electronegative oxygen atom, and the bond is therefore highly polarized. The carbon atom is an electron-deficient acceptor centre, while the oxygen is an electron-excess donor one (Fig. 42). The arrangement of the carbon and oxygen atoms in one plane makes the carbonyl group readily accessible for an attack.

Aldehydes are more reactive than ketones. In the series of compounds given below, the activity drops from formaldehyde to acetone, which can be explained by the influence of the $+I$ effect of the methyl groups on the $\delta+$ charge of the carbon atom:

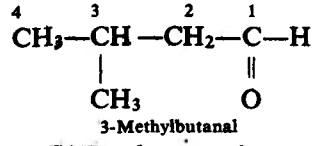


Nomenclature and Isomerism. By the IUPAC nomenclature, aldehydes and ketones are named by replacing the *-ane* ending of the relevant hydrocarbon with *-al* for aldehydes and *-one* for ketones:



Propanal Propanone

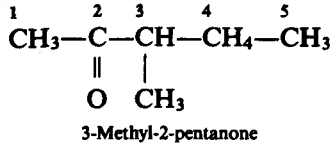
The isomerism of aldehydes is associated with the structure of the hydrocarbon radical. When there is a branched chain, numbering is begun from the aldehyde group carbon:



3-Methylbutanal

and then all the other IUPAC rules are observed.

The isomerism of ketones is determined by the structure of the carbon chain, and also by the position of the carbonyl group. The chain is numbered so as to give the carbonyl group the lowest possible number:

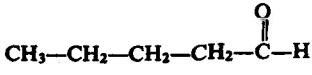


3-Methyl-2-pentanone

The trivial names are widely used for many aldehydes and ketones. A few examples are given in Table 10.

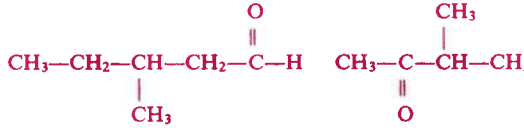
Table 10

IUPAC and Trivial Names of Some Simple Aldehydes and Ketones

Structure	IUPAC name	Trivial name
	Methanal	Formaldehyde
	Ethanal	Acetaldehyde
	Pentanal	Valeraldehyde
	2-Propanone	Acetone
	2-Butanone	Methyl ethyl ketone

Questions and Problems

1. Give the IUPAC names of the following compounds belonging to the class of aldehydes and ketones:

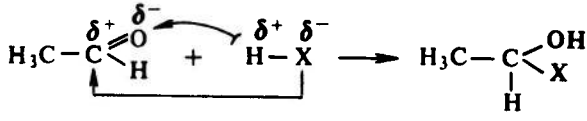


2. Compare the structure of the carbonyl group with ethylene. What are their common and different features?

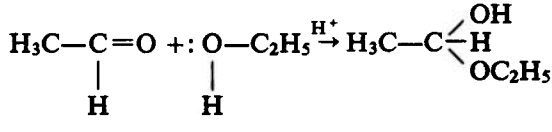
22.2. Properties

Physical Properties. Aldehydes and ketones are polar substances with low boiling and melting points. The explanation is that they are not associated. The lower representatives (formaldehyde, acetaldehyde, acetone) dissolve in water quite readily. All the aldehydes and ketones have typical odours.

Chemical Properties. Addition Reactions. Owing to the high polarization of the $C\overset{\delta+}{=}O\overset{\delta-}{}$ bond, it is readily broken by the action of polar molecules such as $H\overset{\delta+}{-}X\overset{\delta-}{}$. In the general form, this can be depicted as follows:

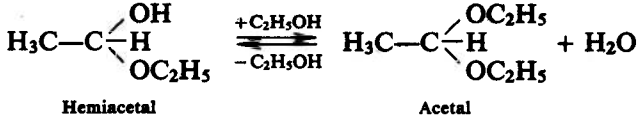


Of a major importance is the reaction of aldehydes and ketones with alcohols, which leads to the formation of **acetals** from aldehydes and **ketals** from ketones. The intermediates in these reactions are hemiacetals and hemiketals. Alcohols are weak nucleophiles, therefore a reaction is catalyzed by acids. The intermediate hemiacetal (hemiketal) next reacts with a second alcohol molecule and transforms into the product—an acetal*:



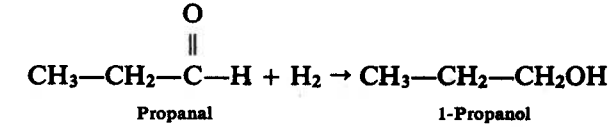
Acetaldehyde Ethanol Hemiacetal

* This reaction is considered in detail because the given material is important for the correct understanding of the chemistry of carbohydrates.

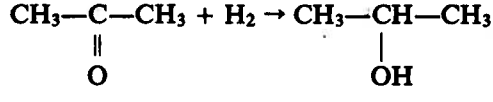


Hemiacetal Acetal

The addition of hydrogen to aldehydes leads to the formation of **primary alcohols**, and to ketones, of **secondary alcohols:**



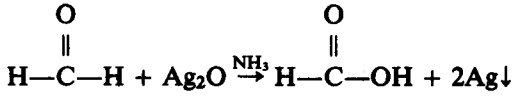
Propanal 1-Propanol



Acetone 2-Propanol

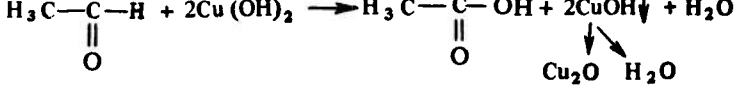
The addition of hydrogen to formaldehyde yields methanol, and to acetaldehyde yields ethanol.

Oxidation Reactions. The oxidation of aldehydes always yields *acids with the same number of carbon atoms as in a molecule of the initial aldehyde.* For instance, if an aldehyde solution is added to an ammonia solution of silver oxide, the aldehyde will be oxidized to an acid with the same number of carbon atoms. Metallic silver will be deposited on the walls of the test tube in the form of a mirror, owing to which this reaction is known as the silver mirror test:



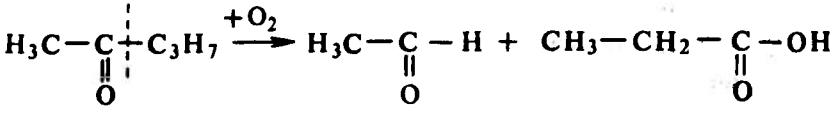
Formaldehyde Formic acid

The reaction of aldehyde oxidation in the presence of copper(II) hydroxide, which is reduced to copper(I) hydroxide, proceeds similarly:



The silver mirror test is negative for ketones because mild oxidizing agents such as Ag_2O do not react with them. Ketones are oxidized in the presence of strong oxidizing agents under rigorous conditions, and this is attended by the cleavage of a C—C bond. Acids form with less carbon

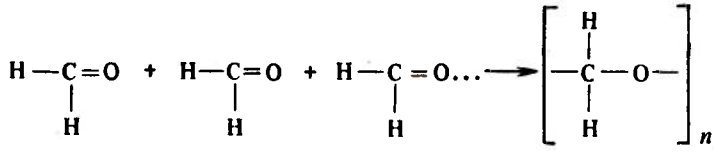
atoms than in the initial ketone. The carbonyl group remains with the radical containing the smaller number of carbon atoms:



2-Pentanone Acetaldehyde Propionic acid

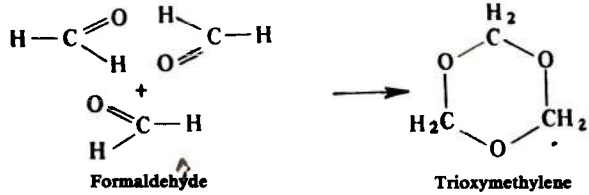
Polymerization Reactions. These are characteristic only of aldehydes. Ketones do not enter into such reactions.

Aldehydes can enter into reactions of both **linear** and **cyclic** polymerization. For example, the polymer called Paraform is obtained from formaldehyde:



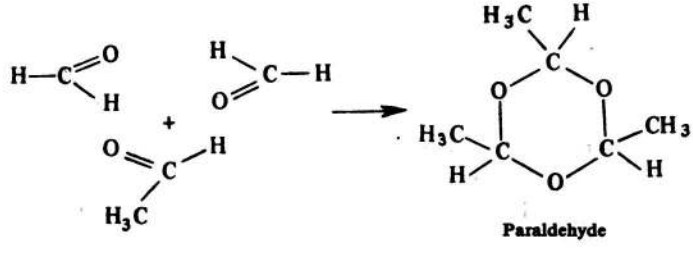
Paraform

Cyclic polymerization yields cyclic trimers:



Formaldehyde Trioxymethylene

Acetic aldehyde polymerizes to form paraldehyde:



Paraldehyde

Questions and Problems

1. What products form in the hydrogenation of aldehydes and ketones and why?
2. Do differences in the properties of aldehydes and ketones with respect to oxidizing agents manifest themselves?
3. Characterize the common and different reactions of aldehydes and ketones.
4. Why is an addition reaction more typical of the carbonyl group?
5. How do hydrocarbon radicals affect the reactivity of the carbonyl group and what is the cause of this influence?
6[a]. To determine the per cent concentration by mass of formaldehyde, an excess of an ammonia solution of silver nitrate was added to the analyte solution and the mixture was heated for some time. The mass of the precipitated silver was 4.32 g. Find the per cent concentration by mass of the formaldehyde in the solution.
7[a]. In the silver mirror test, 0.18 g of an aldehyde reduced 0.54 g of silver. Use these data to determine the formula of the aldehyde.
8[a]. The vapour density of a substance relative to hydrogen was 22. The content of carbon, hydrogen, and oxygen was 54.54, 9.1, and 36.36%, respectively. Determine the formula of the compound.

22.3. Production Methods. Some Representatives

Aldehydes and ketones are produced by the following common methods.

By the oxidation of alcohols:

(a) aldehydes are produced from primary alcohols:

$$\underset{\text{1-Propanol}}{CH_3—CH_2—CH_2OH} \xrightarrow{[O]} CH_3—CH_2—\overset{\overset{O}{\|}}{C}—H$$

(b) ketones are produced from secondary alcohols:

$$CH_3—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow{[O]} H_3C—\overset{\overset{O}{\|}}{C}—CH_3$$

2-Propanol

By the hydration of alkynes under conditions of the Kucherov reaction:

(a) if acetylene is the initial substance, acetaldehyde forms:

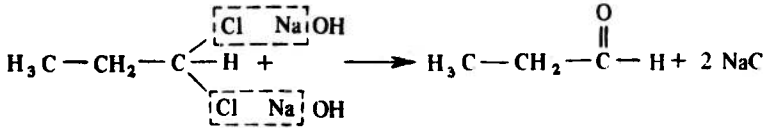
$$HC{\equiv}CH + HOH \xrightarrow{Hg^{2+}} CH_3—\overset{\overset{O}{\|}}{C}—H$$

(b) ketones form from other alkynes under these conditions:

$$\underset{\text{Propyne}}{H_3C—C{\equiv}CH} + HOH \xrightarrow{Hg^{2+}} CH_3—\overset{\overset{O}{\|}}{C}—CH_3$$

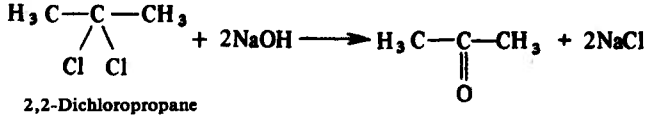
By the hydrolysis of dihalogen derivatives of alkanes:

(a) aldehydes are obtained from primary dihalogen derivatives:



1,1-Dichloropropane

(b) ketones are obtained from secondary dihalogen derivatives:



2,2-Dichloropropane

Formaldehyde (methanal) $H-\overset{\overset{O}{\|}}{C}-H$ is a colourless gas with a typical pungent odour. *It is poisonous.* It dissolves readily in water. A 40% aqueous solution of formaldehyde is called **formalin.** Formaldehyde is produced by the catalytic oxidation of methanol and is chiefly used in the production of plastics, lacquers, varnishes, and glues based on phenolformaldehyde resins.

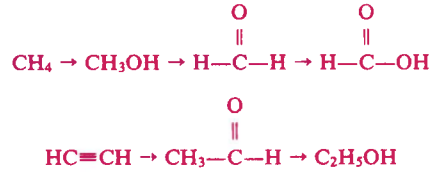
Acetaldehyde (ethanal) $CH_3-\overset{\overset{O}{\|}}{C}-H$ is a colourless transparent liquid with a pungent unpleasant odour boiling at 21 °C. It dissolves well in water. It is produced commercially from acetylene (see the methods of producing aldehydes).

Acetaldehyde is widely used in the organic synthesis industry. It is a raw material for the production of acetic acid, ethyl acetate, ethanol, synthetic resins, etc.

Acetone $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ is a colourless transparent liquid with a typical odour. It dissolves well in water. It is widely used as a solvent of varnishes and lacquers, plastics, rayon, etc.

Questions and Problems

1. Why does acetylene yield acetaldehyde by the Kucherov reaction, while its homologues yield only ketones?
2. How can the following transformations be carried out:



3*. Acetylene produced from calcium carbide was hydrated, and 176 g of acetaldehyde were obtained. How many grammes of the carbide were needed for this if the impurity content in it was 25%?

4*. The formaldehyde produced in the dehydrogenation of methanol was dissolved in water and 100 g of a 9% solution were obtained. How many grammes of the methanol were used if the yield of the formaldehyde was 75% of the theoretical value?

SUMMARY

Aldehydes and ketones belong to carbonyl compounds. The carbonyl group C=O has a high reactivity, which is explained by its structure. The carbon atom is sp^2 hybridized. It is joined to the oxygen by one sigma and one pi bonds as in ethylene. But unlike the ethylene double bond, the bond in carbonyl is highly polarized owing to the shift of the electron cloud to the more electronegative oxygen. Therefore, carbonyl has two reactive centres—an electrophilic one (the carbonyl carbon) and a nucleophilic one—the oxygen atom. The carbonyl group enters into an addition reaction with polar molecules at the expense of breaking of the pi bond. Such reactions are exemplified by the reaction of aldehydes and ketones with alcohols. By adding an alcohol, an aldehyde transforms into a hemiacetal and then, after adding a second alcohol molecule, into an acetal.

Aldehydes and ketones are reduced to primary and secondary alcohols, respectively. In oxidation reactions, aldehydes yield carboxylic acids with the same number of carbon atoms. Aldehydes also enter into polymerization and polycondensation reactions.

CHAPTER 23

CARBOXYLIC ACIDS AND THEIR FUNCTIONAL DERIVATIVES

OBJECTIVES

To know the electron structure of the carboxyl group and the mechanism of its losing a proton; to know the reasons underlying the mobility of the hydrogen and hydroxyl group; the electron structure of the carboxy-

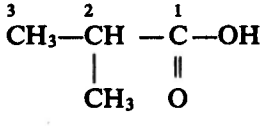
late anion; to discuss the factors affecting the drop in the carbonyl activity of acids in comparison with aldehydes; to consider the most important chemical properties of acids and their functional derivatives; to know the mechanism of the reaction of acids with alcohols, and the properties of esters and fats.

23.1. Monatomic Acids

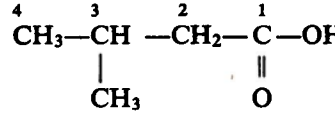
Carboxylic acids are hydrocarbon derivatives in which one or more hydrogen atoms are replaced by the carboxyl group $-C(=O)-OH$.

Depending on the number of carboxyl groups in a molecule, we distinguish monatomic, diatomic, and polyatomic acids.

Nomenclature and Isomerism. The IUPAC nomenclature has retained the trivial names of the simplest acids (Table 11). By the IUPAC system, carboxylic acids are named by changing the ending $-e$ in the name of the parent hydrocarbon to $-oic\ acid$. Isomerism in the acid series depends on the structure of the carbon chain. The same principle is followed in naming acids with a branched chain of carbon atoms as in naming aldehydes, e.g.:



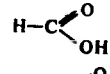
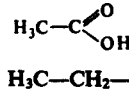
2-Methylpropanoic acid



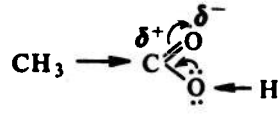
3-Mehylbutanoic acid

Table 11

Selected Representatives of the Carboxylic Acids

Name		Formula	M.p., °C	B.p., °C
IUPAC	Trivial			
Methanoic acid	Formic acid		+8.6	100
Ethanoic acid	Acetic acid		17	118
Propanoic acid	Propionic acid	H_3C-CH_2-COOH	−22	141
Butanoic acid	Butyric acid	$H_3C-CH_2-CH_2-COOH$	−8	165
Pentanoic acid	Valeric acid	$H_3C-(CH_2)_3-COOH$	−34	187
Hexanoic acid	Caproic acid	$H_3C-(CH_2)_4-COOH$	−3	205

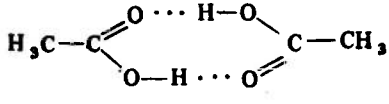
Structure of the Carboxyl Group. The carboxyl group can be considered formally as a combination of a carboxyl and hydroxyl groups. But such an approach is convenient only for describing its composition because the group —COOH is an independent functional group differing in its structure and properties from carbonyl. The primary cause of this difference is that the pi electrons of the $>C=O$ bond interact with the *p* electrons of the hydroxyl group oxygen, and this leads to conjugation. The polarization of the C=O bond sharply grows because of the additional drawing together of the unshared pair of electrons (*p* electrons) of the OH group oxygen atom:



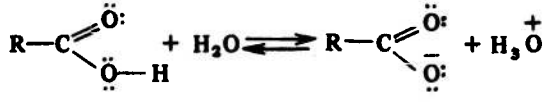
Owing to such a shift of the electron density, the O—H bond in the hydroxyl group weakens, and the hydrogen atom is readily eliminated in the form of an H^+ ion. This is why it is exactly the hydroxyl group that participates in almost all the reactions, namely, it either loses a proton (H^+) or is substituted under the action of nucleophilic reagents.

Another feature of the carboxyl group is that it does not exhibit carbonyl activity (unlike aldehydes and ketones).

Physical Properties. The first three representatives of the homologous series of acids are colourless transparent liquids with a typical pungent odour; they mix with water in any proportions. With a growth in the number of carbon atoms in the radicals of acids, their solubility in water diminishes. Acids containing 10 or more carbon atoms are solids. The high boiling points (see Table 11) indicate the presence of intermolecular hydrogen bonds:

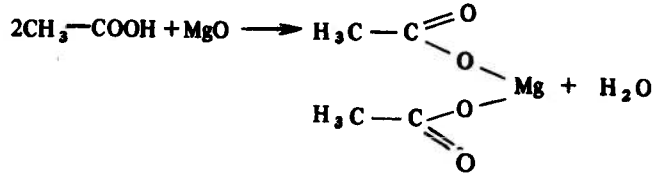


Chemical Properties. Most organic acids are weaker than mineral acids. They dissociate in aqueous solutions as follows:



Carboxylic acids react with active metals, oxides, hydroxides, and salts of weaker acids:

$$2CH_3—COOH + Fe \rightarrow (CH_3—COO)_2Fe + H_2$$



$$H_3C—COOH + KOH \rightarrow H_3C—\overset{\overset{O}{\|}}{C}—OK + H_2O$$

$$H_3C—COOH + NaHCO_3 \rightarrow H_3C—\overset{\overset{O}{\|}}{C}—ONa + CO_2\uparrow + H_2O$$

Aqueous solutions of carboxylic acid salts are strongly hydrolyzed:

$$H_3C—\overset{\overset{O}{\|}}{C}—ONa + HOH \rightarrow H_3C—\overset{\overset{O}{\|}}{C}—OH + NaOH$$

Salt of strong base and weak acid

The carboxyl group activates a hydrogen atom in a radical, especially that joining the carboxyl carbon. As a result, substitution reactions in such radicals are possible:

$$H_3C—\overset{\overset{O}{\|}}{C}—OH + Cl_2 \rightarrow ClCH_2—\overset{\overset{O}{\|}}{C}—OH + HCl$$

Monochloroacetic acid

Carboxylic acids react with alcohols to form **esters** (an esterification reaction). The reaction is catalyzed by acids. When an alcohol reacts with a carboxylic acid, a hydrogen atom is eliminated from the alcohol and a hydroxyl group from the acid:

$$CH_3—\overset{\overset{O}{\|}}{C}—\boxed{OH + H}—OC_2H_5 \rightarrow CH_3—\overset{\overset{O}{\|}}{C}—OC_2H_5 + H_2O$$

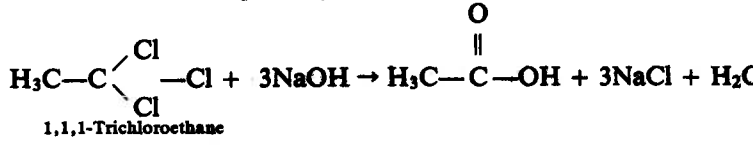
Carboxylic acids react with phosphorus halides to form halogen anhydrides (carboxylic acid halides):

$$H_3C—\overset{\overset{O}{\|}}{C}—OH + PCl_5 \rightarrow H_3C—\overset{\overset{O}{\|}}{C}—Cl + POCl_3 + HCl$$

Acetyl chloride

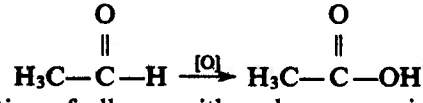
Production. Carboxylic acids can be produced in various ways:

(a) by the hydrolysis of trihalogen derivatives in which all the halogen atoms are bonded to a primary carbon atom:

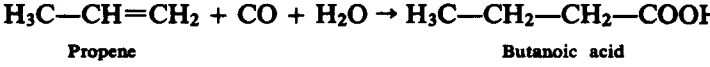


1,1,1-Trichloroethane

(b) by the oxidation of aldehydes:



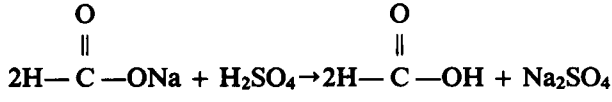
(c) by the reaction of alkenes with carbon monoxide and steam (oxo-synthesis):



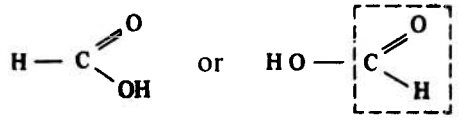
Propene Butanoic acid

Some Representatives. Formic acid (methanoic acid) is a colourless transparent liquid with a typical pungent odour. It is produced commercially from carbon monoxide and sodium hydroxide with the following reaction of the obtained salt with sulphuric acid:



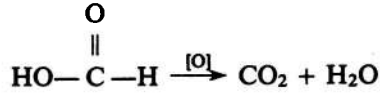


Formic acid differs from the other carboxylic acids in that the carboxylic group in it is attached to a hydrogen atom instead of to a hydrocarbon radical. This is why formic acid can be considered either as an acid or as an aldehyde:



Aldehyde group

Like aldehydes, formic acid can be oxidized:



and this is why formic acid gives positive results in a silver mirror test:

$$HO-\overset{\overset{O}{\|}}{C}-H + Ag_2O \rightarrow HO-\overset{\overset{O}{\|}}{C}-OH + 2Ag\downarrow$$

Formic acid is used in industrial organic synthesis.

Acetic acid (ethanoic acid) is a colourless transparent liquid with a typical pungent odour of vinegar. Anhydrous acetic acid exists in the form of crystals melting at 16.6 °C. This is why such an acid is called glacial acetic acid. It mixes with water in all proportions.

In the industry, acetic acid is produced from acetylene via acetaldehyde (see the Kucherov reaction), by the oxidation of alkanes, or by the oxidation of ethanol.

Acetic acid is widely used in the organic synthesis industry for producing acetic anhydride, ethyl and butyl acetates, dyes, and drugs, and also in the leather industry.

Palmitic acid $C_{15}H_{31}COOH$ and **stearic acid $C_{17}H_{35}COOH$** are very important representatives of the higher fatty acids. They are contained in fats.

Acrylic acid (pentenoic acid) **$CH_2=CH-COOH$** is the simplest representative of the unsaturated acids. Acrylic acid has all the properties of a carboxylic acid. At the same time, the presence of an unsaturated double bond makes it capable of entering into addition and polymerization reactions. For example, acrylic acid and its methyl ester—methyl acrylate (methacrylate) in polymerization form a variety of transparent plastics:

$$CH_2=\underset{\displaystyle COOCH_3}{\underset{|}{CH}} + CH_2=\underset{\displaystyle COOCH_3}{\underset{|}{CH}} + CH_2=\underset{\displaystyle COOCH_3}{\underset{|}{CH}}\ldots \rightarrow -CH_2-\underset{\displaystyle COOCH_3}{\underset{|}{CH}}-CH_2-\ldots$$

$$\ldots-CH-CH_2-\underset{\displaystyle COOCH_3}{\underset{|}{CH}}-\rightarrow \left[-CH_2-\underset{\displaystyle COOCH_3}{\underset{|}{CH}}-\right]_n$$

Polymethacrylate

Polymethacrylate is a transparent glassy substance known as organic glass.

Oleic acid $C_{17}H_{33}COOH$ is an unsaturated higher fatty acid. It is a constituent of oils. It contains one unsaturated bond in its radical:

$$CH_3-(CH_2)_7-\overset{10}{CH}=\overset{9}{CH}-(CH_2)_7-\overset{1}{COOH}$$

Questions and Problems

1. Explain the electron structure of the carboxyl group.
2. What ways of breaking the bonds are possible in the COOH group? What is the cause of each way?
3. Why are the acidic properties of the carboxylic acids much higher than those of alcohols?
4. How does the presence of substituents in the hydrocarbon radical affect the acid properties?
5. Give examples of specific reactions for achieving the transformations corresponding to the following scheme:

$$C_nH_{2n+2} \rightarrow R{-}OH \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}H \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}OH \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'$$

Name all the substances participating in the reactions and indicate the conditions under which the reactions proceed.

6*. Determine the composition and structure of a monatomic carboxylic acid if 10 g of a 2% NaOH solution are needed to neutralize 0.37 g of it.

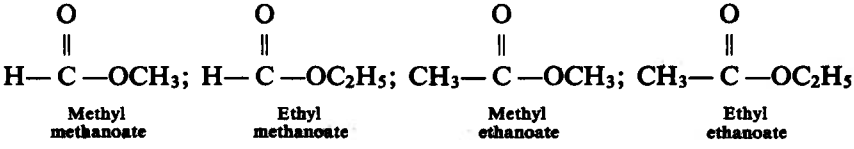
7*. The oxidation of acetaldehyde yielded 40 g of a 25% acetic acid solution. What mass of the aldehyde was oxidized?

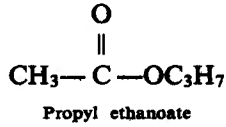
8*. To neutralize 20 g of a solution containing formic and acetic acids, 20 g of a 20% NaOH solution were needed. When an identical mass of the solution of acids was reacted with an ammonia solution of silver nitrate, 10.8 g of silver were obtained. What was the per cent concentration by mass of each of the acids in the solution?

9*. The Kucherov reaction was used to produce acetaldehyde from acetylene; the acetaldehyde was then reduced to ethanol. What volume of acetylene was spent for producing 73.6 g of ethanol if the yield of the aldehyde was 75% and of the ethanol 80% of the theoretical value?

23.2. Esters

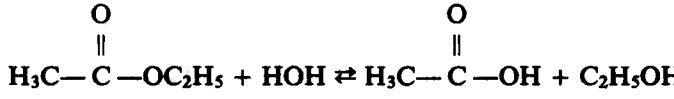
Esters are obtained when alcohols react with acids. The names of esters are formed from those of the acids and alcohols participating in the formation of their molecules. For instance, the ester formed by formic acid $H{-}\overset{\overset{O}{\|}}{C}{-}OCH_3$, by acetic acid and $CH_3{-}\overset{\overset{O}{\|}}{C}{-}OC_2H_5$, etc. By the IUPAC nomenclature, the names of esters, like those of salts, are formed using the IUPAC names of the acids and changing the *-ic* ending of the latter to *-ate*. The name of the alcohol radical is indicated first:



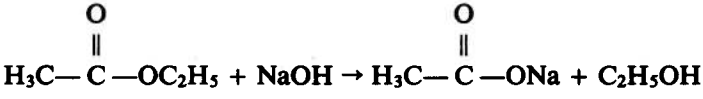


Physical Properties. Esters formed by lower representatives of acids and alcohols are liquids. They have a pleasant odour reminding one of fruit. The esters dissolve very sparingly in water, and readily in organic solvents.

Chemical Properties. The reaction of hydrolysis (saponification) of esters is the reverse reaction to esterification. The process can occur in both an acid and an alkaline medium. The reaction is reversible in the presence of acids because the formed acid and alcohol again react to produce an ester:



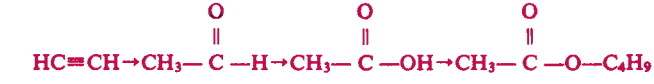
In the presence of an alkali, the reaction is irreversible because the formed acid is neutralized by the alkali:



Questions and Problems

1. Write the equation of the esterification reaction between acetic acid and 2-propanol. Name the product.

2. How can the following transformations be carried out:



3*. What mass of acetaldehyde is needed to produce 32 g of ethyl acetate?

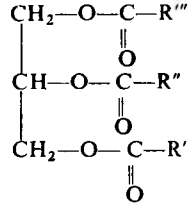
4*. How many grammes of ethyl acetate can be obtained from 15 g of acetic acid and 20 g of ethanol if the yield of the ester is 75% by mass of the theoretical value?

5*. How many grammes of acetic acid and ethanol are needed to produce 17.6 g of ethyl acetate if the yield is 100%?

6*. A portion of 22 g of ethyl acetate was mixed with water and heated for a while. The ester residue was separated using a separatory funnel. The aqueous fraction was neutralized by 40 g of a 12.5% NaOH solution. What was the content of the decomposed ester in per cent by mass of the initial amount?

23.3. Fats and Oils

Fats and oils should be considered as mixtures of esters formed by glycerol and higher fatty acids. The general formula of a fat or oil is:



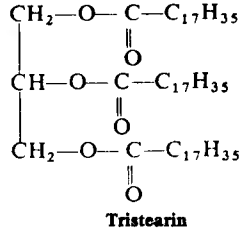
where R′, R″, and R‴ are radicals of the higher fatty acids.

Glycerol is a constant constituent part of natural fats and oils. Up to 50 various acids are contained in fats and oils. In fats, which are generally solid, saturated higher fatty acids predominate, while in oils, which are generally liquid, unsaturated ones are the rule.

The most important acids contained in fats and oils include the following:

$C_{15}H_{31}COOH$—palmitic $C_{17}H_{35}COOH$—stearic	saturated
$C_{17}H_{33}COOH$—oleic $C_{17}H_{31}COOH$—linoleic $C_{17}H_{29}COOH$—linolenic	unsaturated

The glycerol residue in fats and oils is generally bonded to three residues of higher fatty acids. Such completely substituted glycerol esters are called **triacyl glycerides.** An example is:

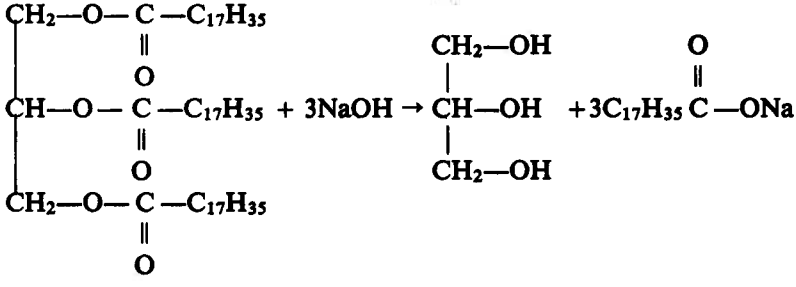


Tristearin

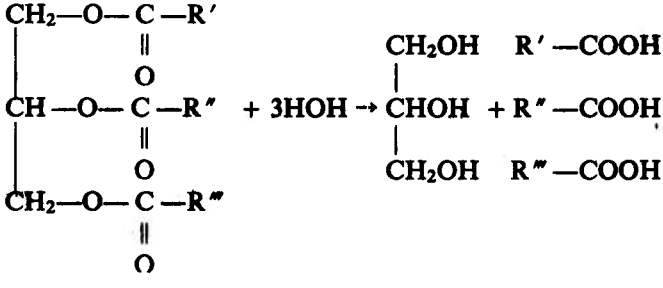
Physical Properties. Oils are chiefly encountered in plants, which is why they are called vegetable oils (an exception is cod liver oil). Most organic fats are found in animals (beef fat, lard, etc.).

Fats and oils mix very poorly with water. They dissolve well in organic solvents such as diethyl ether and petroleum ether.

Chemical Properties. The action of alkali solutions causes alkaline hydrolysis or saponification of fats and oils. The products are glycerol and salts of the relevant higher fatty acids contained in the fat or oil:

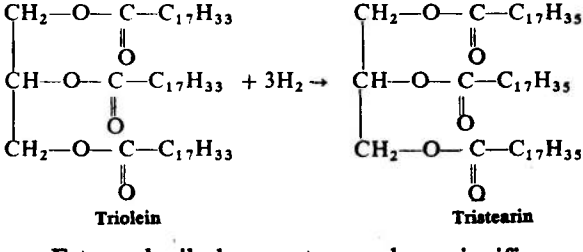


The alkaline hydrolysis of a fat or oil is costly, however. Hydrolysis by the method proposed by G. Petrov is used to replace alkalies. In this case, hydrolysis is performed at a high temperature and pressure in the presence of catalysts—sulphoacids—that simultaneously easily emulsify the fat or oil. The saponification products by this method are glycerol and free fatty acids:



The hydrogenation of fats and oils is a process of adding hydrogen to the residues of the unsaturated fatty acids in them.

In this way, oils are transformed into fats, which are used in the production of margarine—a valuable substitute of butter. The hydrogenation reaction follows the equation:



Fats and oils have a tremendous significance as food products.

Questions and Problems

1. Why are fats and oils called esters?
2. Disclose the biological importance of fats and oils.
3*. Write the formula of the triglyceride formed by oleic, palmitic, and stearic acids. How many grammes of glycerol can be obtained in the hydrolysis of 100 g of such a fat?
4*. Calculate the volume of hydrogen required for the hydrogenation of 100 g of a triglyceride formed by oleic acid.

SUMMARY

The carboxyl group is the functional group determining the chemistry of carboxylic acids. It can be considered as a combination of a carbonyl and hydroxyl group influencing each other by transferring their electron effects. The mutual influence of these groups sharply lowers the carbonyl activity and increases the mobility of the hydrogen in the hydroxyl group. As a result, the carboxyl can eliminate a hydrogen ion H^+ with the formation of a carboxylate anion. The latter is featured by its stability. The carboxyl group is monatomic.

The hydroxyl group, in turn, affects the carbonyl group so that the positive charge on the carbon atom is much lower than is observed in aldehydes. This is why the carbonyl activity in carboxyl is sharply diminished in comparison with aldehydes. The hydroxyl group is also mobile—it is readily replaced by nucleophilic particles. Carboxylic acids react with active metals, oxides, and hydroxides to form stable salts.

When the hydroxyl group is replaced by an alcohol residue (alkoxy group), an ester is obtained.

Esters easily hydrolyze in an aqueous or aqueous-alkaline medium.

The esters of the triatomic alcohol glycerol and the higher fatty acids are called fats and oils. Their state of aggregation is determined by the acid composition, namely, the predomination of unsaturated higher fatty acids is a feature of oils. The predomination of saturated higher fatty acids is a feature of fats. The hydrolysis of a fat or oil yields glycerol and fatty acids. A hydrogenation reaction is used to transform oils into fats.

CHAPTER 24

AMINES

OBJECTIVES

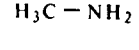
To know the electron structure of amines, be able to explain what determines their basic properties, and also to show the relation between the structure of a radical and the basic properties; to know the reactions of synthesis of secondary and tertiary amines from primary ones, the features of the structure of aniline, and the Zinin reaction; to be able to explain how the amino group affects the reactivity of the aromatic ring in aniline.

24.1. Classification, Nomenclature, and Structure

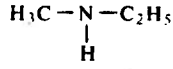
Amines are ammonia derivatives in which the hydrogen atoms are replaced by hydrocarbon radicals.

Aliphatic, aromatic, and **mixed** amines are distinguished. The first type is formed by radicals with an open chain (the aliphatic series), and the second by aromatic radicals. If radicals of both types are attached to an amino group, mixed amines form. Depending on the number of hydrocarbon radicals, regardless of their nature, amines are divided into **primary** ($R—NH_2$), **secondary** ($R—\overset{\overset{H}{|}}{N}—R_1$) and **tertiary** ($R—\overset{\overset{R_2}{|}}{N}—R_1$) ones:

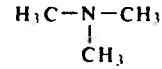
Aliphatic Amines



Methylamine

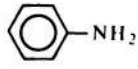


Methylethylamine

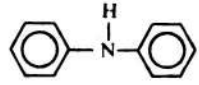


Trimethylamine

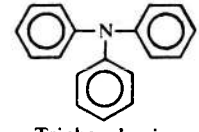
Aromatic Amines



Phenylamine



Diphenylamine

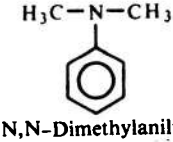


Triphenylamine

Mixed Amines

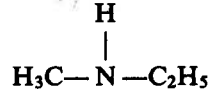


N-Methylaniline



N,N-Dimethylaniline

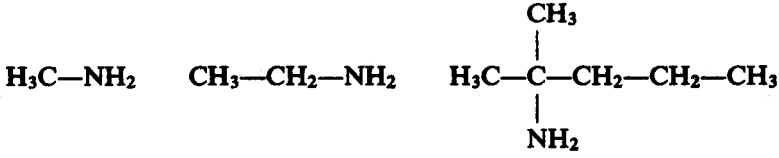
Amines are commonly named in accordance with the radicals they contain by adding the word *amine.* When the radicals attached to the nitrogen atom have different numbers of carbon atoms, the radicals are listed in the order of the increasing number of carbon atoms:



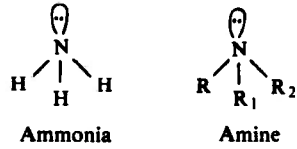
Methylethylamine

The IUPAC system treats amines as derivatives of hydrocarbons, therefore the word amine is preceded by the name of the radical and the position

of the amino group:



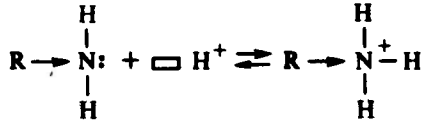
The structure of amines is close to that of ammonia. The nitrogen atom has an unshared pair of electrons that determines the nucleophilic (basic) properties of the amines:



The basic properties grow when going over from ammonia to amines of the aliphatic series. The reason is that the radical, being a donor of electrons, shifts the electron density in the direction of the nitrogen. Hence, the unshared pair of electrons becomes more accessible for interaction with a proton. Amines, like ammonia, attach a proton and transform into a substituted ammonium ion:

$$H_3C—\ddot{N}H_2 + H^+ \rightarrow H_3C—\overset{+}{N}H_3$$

This process follows a donor-acceptor mechanism. Alkyl radicals spread out the positive charge in the formed ion and thus stabilize the latter. In other words, a substituted ammonium ion is stabilized owing to the supply of electrons by alkyl substituents:



Aromatic amines are weaker bases than aliphatic ones. Let us consider aniline. The amino group is joined to the aromatic ring and, being an electron donor, supplies electrons to the benzene ring. The unshared pair of electrons of the amino group interacts with the pi system of the benzene ring to form a single electron cloud. Because of such interaction, the unshared pair of nitrogen electrons is less accessible for the formation of a bond with the H^+ ion.

Questions and Problems

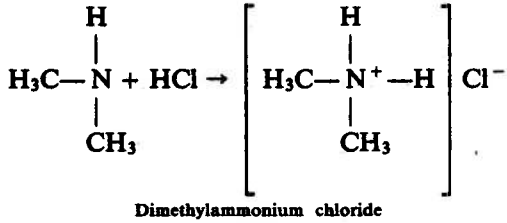
1. Compare the structure and properties of ammonia, methylamine, and aniline. What explains the similarity and difference in their properties?
2. Compare the properties of methylamine and dimethylamine.
3. Do the basic properties of aniline differ from those of methylamine? Defend your answer.

24.2. Properties and Production

Physical Properties. The lower aliphatic amines—methylamine, dimethylamine, and trimethylamine—are gaseous substances readily soluble in water and having the odour of ammonia. The other amines of this series are liquids. The simplest aromatic amine—aniline—is a liquid with a characteristic unpleasant smell. It dissolves sparingly in water.

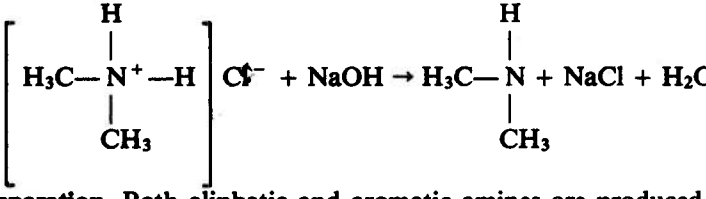
Chemical Properties. The unshared pair of electrons in the nitrogen atom determines the nucleophilic properties of the amines.

When they react with acids, they attach a proton and form salts of substituted ammonium:



Dimethylammonium chloride

The formed salt under the action of a stronger base again transforms into the amine:

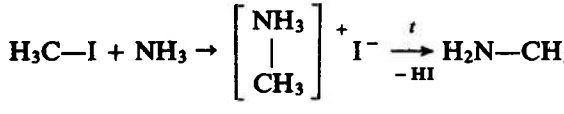


Preparation. Both aliphatic and aromatic amines are produced in the same ways, the most important of which are:

(a) the reduction of nitro compounds:

$$R{-}NO_2 + 6H \rightarrow R{-}NH_2 + 2H_2O$$

(b) the alkylation of ammonia and amines:



(c) the oxidizing decomposition of acid amides:

$$\underset{\text{Propyl amide}}{H_3C-CH_2-\overset{\overset{O}{\|}}{C}-NH_2} + NaOBr \rightarrow \underset{\text{Ethylamine}}{H_3C-CH_2-NH_2} + CO_2 + NaBr$$

Aniline. It was discovered in 1840 by the Russian academician Fritzsche, who produced it by distilling indigo with potassium hydroxide. Indigo is called *anil* in Spanish, hence the name aniline.

In 1842, the Russian organic chemist N. Zinin was the first to develop a method of synthesizing aniline from nitrobenzene, thus giving start to the rapid development of the aniline dye industry. The reaction of aniline synthesis from nitrobenzene is called the **Zinin reaction:**



Nitrobenzene Aniline

The subsequent development of the chemistry of nitrogen-containing aromatic compounds showed how great the significance of this reaction is as a possible way of synthesizing the most important classes of aromatic compounds.

The reactions considered above for amines are characteristic of aniline. It reacts with acids to form salts:

$$\underset{\text{Aniline chloride}}{C_6H_5-NH_2 + HCl \rightarrow [C_6H_5-\overset{+}{N}H_3]Cl^-}$$

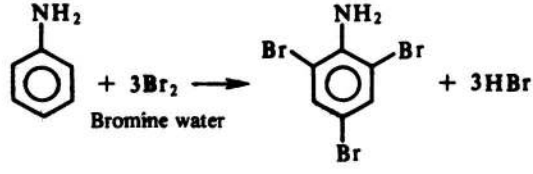
Being a primary amine, aniline enters into a reaction with alkyl halides. Secondary or tertiary amines may form depending on the molar ratio of the reactants:

$$C_6H_5-NH_2 + CH_3I \xrightarrow[-HI]{t} C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{\underset{|}{\overset{|}{N}}}}$$

$$C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{\underset{|}{\overset{|}{N}}}} + CH_3I \xrightarrow[-HI]{t} C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{N}}}}$$

The amino group as a donor of electrons causes the electron density to be shifted in the aromatic ring so that a certain excess of electrons is observed in the 2- (*ortho*-) and 4- (*para*-) positions. This is why substitution reactions in the aromatic ring will occur chiefly in these positions.

A reaction with bromine water forms a tribromoaniline precipitate quite readily. This is used for the qualitative identification of aniline:



The industrial uses of aniline include the synthesis of important organic compounds such as dyes and drugs. An example of a drug produced from aniline is sulphanilamide.

Questions and Problems

1. Write an equation of a reaction of transforming ethylamine into a secondary amine.

2[a]. Bromine water was added to an aniline solution. The precipitate formed had a mass of 1.65 g. How many grammes of aniline did the solution contain?

3[a]. The reduction of 12.3 g of nitrobenzene yielded 8 g of aniline. What per cent did this form of the theoretically possible yield?

4[a]. Benzene participated in a nitration reaction, and the product was reduced with the obtaining of 18.6 g of aniline. How many grammes of benzene were needed for the reaction?

5[a]. Five grammes of aniline chloride were dissolved in 95 g of water. What per cent concentration by mass did this correspond to?

6[a]. Bromine water was treated with 50 g of a mixture of benzene, phenol, and aniline. The mass of the precipitate formed was 9.91 g. When metallic sodium was reacted with the same mass of the mixture, 0.112 lit of hydrogen evolved. What was the per cent concentration by mass of the mixture?

SUMMARY

Amines are organic derivatives of ammonia. They are considered as products obtained by substituting radicals for the hydrogen atoms in ammonia. The electron structure of amines is similar to ammonia. The nucleophilic (basic) properties of aliphatic amines are more pronounced than in ammonia. This is explained by the influence of the electron-donor alkyl radicals stabilizing the positive charge on the ammonium ion.

Aromatic amines have weaker basic properties. The nucleophilic properties of amines are the cause of their reactivity when reacting with alkyl halides. These reactions are attended by the formation of an intermediate stable salt of substituted ammonium that when heated eliminates the hydrogen halide and transforms into the base of the newly formed amine.

CHAPTER 25

AMINO ACIDS. PROTEINS

OBJECTIVES

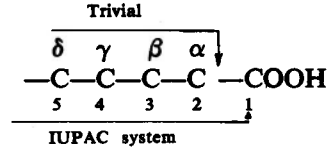
To know the structure of amino acids and their acid-base properties; to become acquainted with the mechanism of bipolar ion formation and polypeptide formation; to know the structure and properties of proteins.

25.1. Amino Acids

Amino acids are hydrocarbon derivatives in whose molecule the hydrogen atoms have been replaced by a carboxyl group COOH and an amino group NH_2.

Amino acids can also be considered as derivatives of acids in whose radical a hydrogen atom has been replaced by an amino group.

The trivial or common names of the amino acids are in general use and in this case the position of the amino group relative to the carboxyl one is designated by letters of the Greek alphabet:



The simplest amino acid formed from acetic acid $CH_2(NH_2)—COOH$ is called glycine; the acid derived from propionic acid and containing the amino group at position 2 (the α carbon atom) is called alanine, etc.

By the IUPAC system, the amino acids are named after the relevant carboxylic acid with the addition of the prefix *amino-*. The position of the amino group is indicated by the corresponding number:

$CH_3—CH(NH_2)—COOH$ — 2-aminopropanoic acid (α-aminopropionic acid)

$CH_3—CH(NH_2)—CH_2—COOH$ — 3-aminobutanoic acid (β-aminobutyric acid)

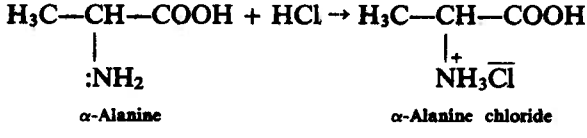
$CH_3—CH(NH_2)—CH_2—CH_2—COOH$ — 4-aminopentanoic acid (γ-aminovaleric acid)

From a biological viewpoint, the α-amino acids, which are structural components of proteins, are of the greatest significance.

Physical Properties. Amino acids are colourless crystalline substances melting at rather high temperatures (200-320 °C), often with decomposition. They dissolve in water; most of them are insoluble in organic solvents.

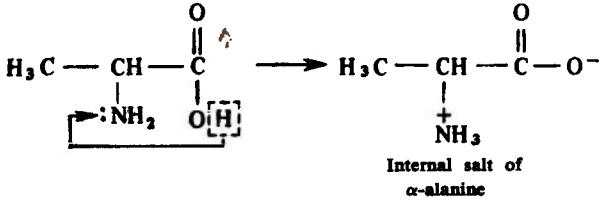
Chemical Properties. Amino acids should be considered as compounds with mixed functions. This is explained by the typical properties of the carboxyl group being exhibited, on the one hand, and the properties of the amino group, on the other. The properties of the carboxyl group were treated in Chap. 23. They include the formation of salts and esters.

The amino group gives rise to basic properties, which is explained by its structure. The properties of the amino group are reflected in reactions with the participation of amino acids. For instance, when reacting with HCl, they form chlorides:



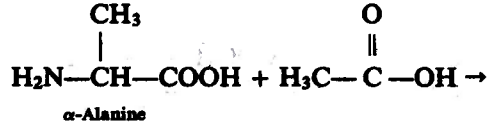
Consequently, having in view the properties of the carboxylic group (acidic properties), on the one hand, and those of the amino group (basic properties), on the other, it is easy to understand that *amino acids have amphoteric properties.*

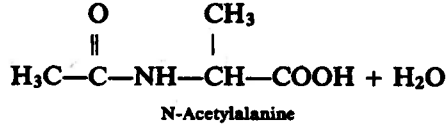
Amino acid solutions have a neutral reaction with litmus: when dissolved in water, the amino group interacts with the carboxylic group in the same molecule to form an internal salt:



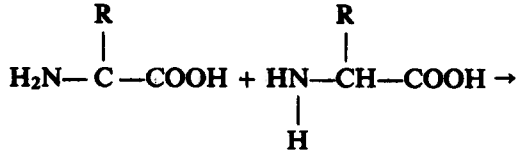
The internal salt of an amino acid is called a **bipolar ion** because the ion has two opposite charges, i.e. two poles.

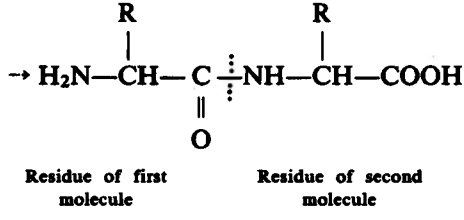
An important reaction of amino acids is their ability to interact with carboxylic acids. In these reactions, one hydrogen atom of the amino group is replaced by a carboxylic acid (acyl) residue. This reaction can be represented in the general form as follows:





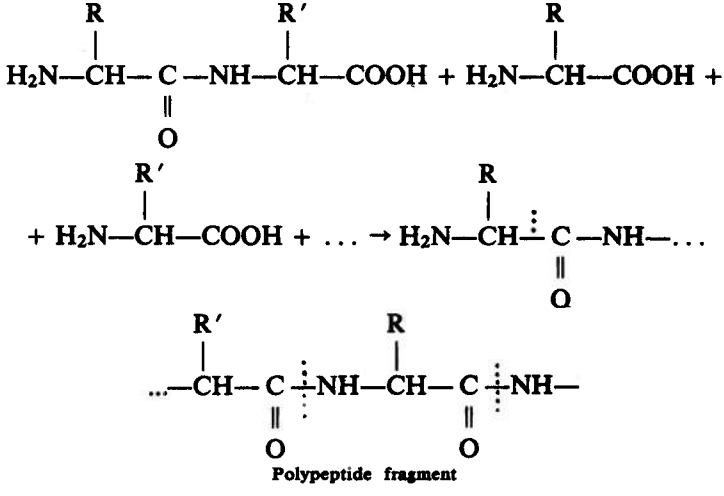
A feature of this reaction is the fact that, for example, the carboxylic group of the first molecule reacts with the amino group of the second one. The carboxyl of the second molecule reacts with the amino group of the third molecule, etc.







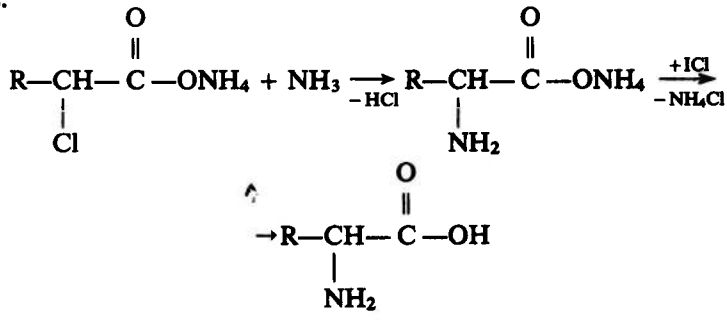
The group is called an **amido** group. If an amido group has been formed with the participation of α-amino acids, it is called a **peptide** one. Compounds obtained in the reaction of two α-amino acids are called **dipeptides.** The latter, like the initial α-amino acids, contain one each of a free carboxyl and amino group. A dipeptide can react by its carboxyl group with the amino group of a third molecule to form a **tripeptide.** A further reaction can occur in the same order with a fourth molecule, and so on. In the long run, a **polypeptide** forms:



The name peptide underlines the relation of these compounds to peptones—products of the partial decomposition of proteins.

Production. The most important way of producing α-amino acids is the hydrolysis of proteins. The formed mixture of various α-amino acids is subsequently separated by physicochemical methods.

The reaction of ammonia with salts of halogen-substituted carboxylic acids has come into favour among the methods of synthesizing amino acids:



Questions and Problems

1. Explain the structural features of amino acids.
2. Why do amino acids have amphoteric properties?
3. What happens in aqueous solutions of amino acids?
4. What properties does a bipolar ion have?
5. Write the equation of the reaction of α-aminopropionic acid with hydrogen chloride.
6. What products form when aminoacetic acid reacts with methyl iodide and with ethanol? Write the reaction equations.
7. Write the formula of the dipeptide formed by aminoacetic and α-aminopropionic acids.

25.2. Proteins

It is considered conditionally that peptides having a relative molecular mass up to 10 000 should be called **polypeptides**, while those with a higher relative molecular mass should be called **proteins.** The name protein originates from the Greek *proteios*—primary. This name is justified because proteins are the basis of all living matter, and are contained in all the cells and tissues of an organism. Proteins perform the most diverse functions.

All natural proteins contain five chemical elements, the amount of which in various proteins is quite close and fluctuates within insignificant limits: carbon—50-53%, hydrogen—7-8%, oxygen—20-24%, nitrogen—16-18%, and sulphur—0.5-1.8%.

In their chemical composition, proteins are divided into two main groups. Proteins in whose hydrolysis only amino acids form are called **simple** ones. Simple proteins, in turn, are distinguished in accordance with their solubility.

If a simple protein is attached to a non-proteinic substance, such proteins are called **conjugated** ones. The latter are classified and named in accordance with their non-proteinic component.

With respect to the shape of their molecules, all proteins are divided into two large groups: **fibrous** (rod-like) and **globular.**

Fibrous proteins consist of chains of polypeptides mainly joined by a hydrogen bond with the formation of complicated helical structures called the **secondary structure of a protein** (Fig. 43).

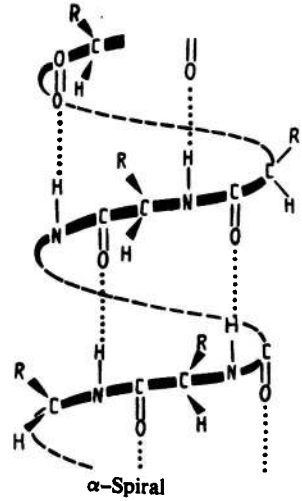


Fig. 43
The secondary structure of peptides and proteins

Some amino acids in addition to the $-NH_2$ and $-COOH$ groups include other functional groups that do not participate in the formation of the polypeptide chain of the primary protein structure. Owing to the interaction of such groups with one another from various polypeptide chains, the **tertiary structure of a protein** is formed.

It is very difficult to establish the structure of proteins because their properties depend not only on the amino acid composition, but also on the sequence of amino acid joining in a protein molecule. Moreover, the proteins of every living organism have their own specific features.

A molecule of a globular protein has a cylindrical shape; the diameter of the cylinder may be equal to its altitude.

The physical and chemical properties of proteins depend on their structure.

Some proteins (e.g., pepsin, egg albumin) can be obtained in the crystalline form, but most proteins are amorphous substances having no definite boiling and melting points.

The action of high temperatures and also of heavy metal salts destroys the secondary and tertiary structures of proteins. Here **denaturation** of a protein occurs, i.e. it loses its ability to dissolve in water. It also loses its biological activity. At a still higher temperature, proteins become charred, which is attended by the appearance of a smell of burnt animal horn.

A very important chemical property of proteins is their hydrolysis that causes molecules to break up into their components.

Typical qualitative reactions based on the formation of coloured products are used to identify proteins.

Questions and Problems

1. What is the relation between the properties of amino acids and the formation of a protein molecule?
2. How can the following transformations be carried out:

$$C_2H_6 \rightarrow C_2H_5OH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-H \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH \rightarrow$$

$$\rightarrow NH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH \rightarrow NH_2-CH_2-\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

SUMMARY

Amino acids are derivatives of carboxylic acids in whose radical a hydrogen atom has been replaced by an amino group.

Amino acids belong to bifunctional compounds: their basic properties are due to the amino group, and their acidic properties to the carboxyl

group. Aqueous solutions of monatomic monoamino acids are neutral. This feature is associated with the formation of an internal salt—the proton from the carboxyl attaches to the amino group. Such an internal salt has the structure of a bipolar ion.

A feature of α-amino acids is their ability to react with one another, forming a peptide bond. In a dipeptide (a compound of two amino acids), one of the amino acid residues has a free amino group, and the other has a free carboxyl group, therefore it can react with a third amino acid to form a tripeptide, and so on. Polypeptides are contained in proteins.

CHAPTER 26

CARBOHYDRATES

OBJECTIVES

To know the classification of carbohydrates; the structure of monosaccharides; to consider the formation of cyclic hemiacetal forms of monosaccharides; to know the features of hemiacetal hydroxyl; to learn the properties of glucose, the structure of saccharose, starch, and cellulose.

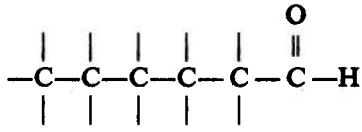
26.1. Monosaccharides

Carbohydrates are a very important class combining a broad group of natural compounds of a plant and animal origin.

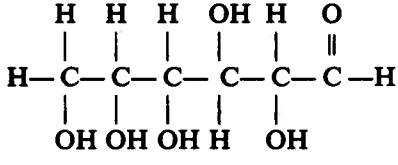
The origin of the term **carbohydrate** is associated with the fact that the first known representatives correspond to the formula $C_mH_{2n}O_n$ or $C_m(H_2O)_n$ and were formally treated as **carbon hydrates.** Although the above formula $C_mH_{2n}O_n$ does hold for the overwhelming majority of the representatives of this class, nevertheless as regards their structure they cannot be considered as "carbon hydrates". Carbohydrates are divided into two groups: **simple carbohydrates (monosaccharides)** and **complex carbohydrates (polysaccharides).**

The name monosaccharides is applied to carbohydrates that cannot break up into simpler ones. Most monosaccharides contain the same number of carbon and oxygen atoms. Monosaccharides containing an aldehyde group are called **aldoses,** and those containing a keto group—**ketoses.** The number of carbon atoms is indicated by using the relevant Greek prefixes. For instance, glucose $C_6H_{12}O_6$ relates to hexoses.

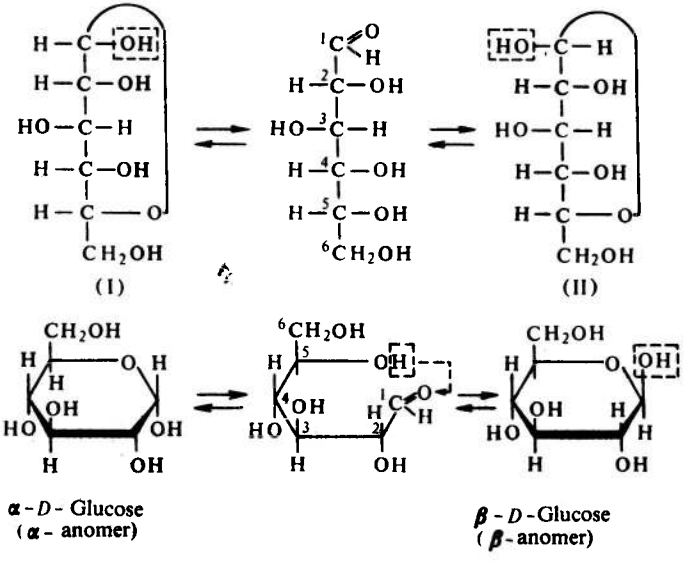
Glucose and **fructose** are the most widespread among the monosaccharides. Glucose contains an aldehyde group that can be formed only at the expense of a terminal carbon atom:



Another important property of glucose is its ability to react with copper(II) hydroxide, which is typical of polyatomic alcohols. Consequently, glucose is an aldehyde-alcohol containing five hydroxyl groups:



In addition to the acyclic form, glucose and other monosaccharides can exist in cyclic forms. It is easy to understand the formation of a cyclic form proceeding from the structure of a glucose molecule: the carbon chain is bent and therefore the hydroxyl group at the fifth carbon atom is close to the aldehyde group. The hydrogen of the OH group attaches to the carbonyl hydrogen to form an **intramolecular hemiacetal** (two functional groups—the alcohol OH and C=O—interact in one molecule):

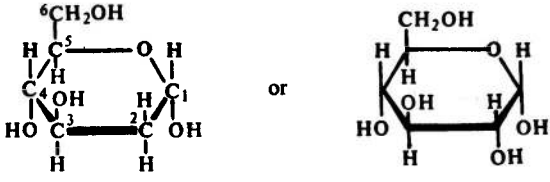


The hydroxyl group formed in this case is called a **hemiacetal hydroxyl** (in the cyclic form it is at the C_1 atom and is designated by a dashed frame).

It is convenient to depict cyclic forms of saccharides by using perspective

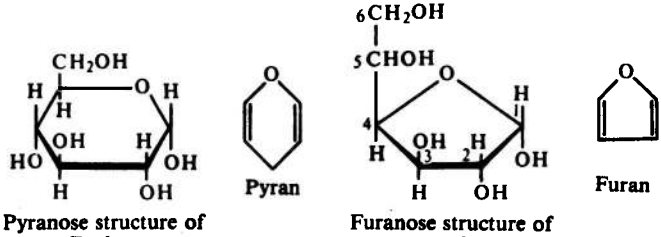
images of the structures illustrating the mutual arrangement in space of the hydroxyl groups (the Haworth projection). To show the position of the ring plane, the three bonds joining the carbon atoms facing the reader are designated by thick lines.

In Haworth projections, the symbols of the carbon atoms are usually not written out:



In the cyclic form of the same monosaccharide, the hemiacetal OH group can be arranged differently in space, producing alpha and beta forms called **anomers.**

Monosaccharides exist chiefly in the form of cyclic hemiacetals. In glucose, the oxygen-containing ring may be six-membered or five-membered, which is structurally similar to the oxygen-containing heterorings pyran and furan. This is why these cyclic forms of glucose are called **pyranose** and **furanose** ones, respectively:



Pyranose structure of α-D-glucose (α-D-glucopyranose)

Furanose structure of α-D-glucose (α-D-glucofuranose)

The cyclic and aldehyde forms are in equilibrium with each other. Hence, reactions are possible that are typical of the aldehyde and cyclic forms. For example, the silver mirror test and the reduction of $Cu(OH)_2$ give positive results only with the aldehyde form, while reactions typical of glucose as a polyatomic alcohol (the formation of ethers and esters, copper saccharate similar to glycerate, etc.) can proceed with the cyclic form. It is exactly the cyclic form that participates in the formation of di- and polysaccharides.

Glucose is oxidized very readily under mild conditions with the formation of gluconic acid. The latter, like glucose, contains six carbon atoms:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{[O]} \underset{\text{Gluconic acid}}{C_6H_{12}O_7}$$

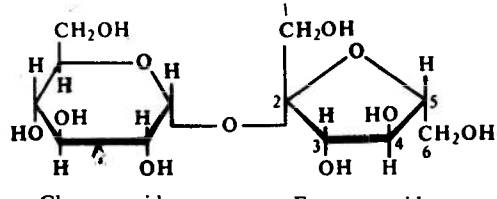
A reaction of reduction of the aldehyde group is possible with the formation of a hexatomic alcohol.

Questions and Problems

1. Compile equations of reactions characterizing glucose as (a) an aldehyde, and (b) a polyatomic alcohol.
2. Of what significance is the fermentation of glucose?
3. List the compounds having mixed functional groups that you know and write equations of reactions characterizing each of these groups.
4. Write the structural formula of the ester formed by glucose and acetic acid.
5*. In the alcohol fermentation of glucose, 161 g of ethanol were obtained. How many grammes of glucose were needed?
6*. What volume is occupied by the CO_2 evolved in the fermentation of 450 g of glucose?
7*. How many grammes of acetic acid are required for the complete acetylation of 36 g of glucose?

26.2. Di- and Polysaccharides

Saccharose (cane or beet sugar) is a disaccharide. Its molecule consists of two monosaccharides: α-D-glucose and β-D-fructose. This signifies that the hemiacetal hydroxyl of glucose has reacted with the hemiacetal hydroxyl of fructose with the separation of water. The structural formula of saccharose can be written as follows:



Glucose residue Fructose residue

The hydrolysis of saccharose yields a molecule each of glucose and fructose:

$$\underset{\text{Saccharose}}{C_{12}H_{22}O_{11}} \xrightarrow{+HOH} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Saccharose occurs abundantly in nature and is contained in sugar cane, beets, and corn. It is an important food product.

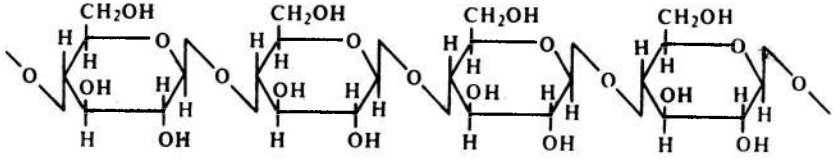
Starch $(C_6H_{10}O_5)_n$ is one of the most abundant polysaccharides. It is encountered in virtually all plants, playing the role of a reserve nutrient substance. A product of the complete hydrolysis of starch is α-D-glucose.

In acid and enzymatic hydrolysis, starch decomposes into several intermediates consisting of a smaller number of glucose residues. A typical reaction for starch is that with iodine attended by the formation of a blue product. This reaction is often used to control the course of starch hydrolysis. As the starch molecules decompose and products with a lower relative molecular mass form, the blue colour gradually transforms to a red one, and then, when the hydrolysis reaction terminates, the solution loses its colour completely:

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \rightarrow \underset{\text{Dextrins}}{(C_6H_{10}O_5)_x} \rightarrow \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Starch is thus a polysaccharide built up of α-D-glucose residues. The giant starch molecules consist of two types of polysaccharides, namely, better soluble in water—**amylose** (20%) and more poorly soluble in water — **amylopectin** (80%). Both consist of glucose residues, but joined differently to one another.

Cellulose $(C_6H_{10}O_5)_n$ is a polysaccharide present in the supporting tissues of plants. Cellulose, like starch, is a polymer formed of glucose structural units. But unlike starch, cellulose is built up of residues of β-D-glucose:



Fragment of cellulose molecule

The relative molecular mass of cellulose varies from 150 000 to 1 000 000.

The chemical processing of cellulose yields industrially important products. Of special interest are cellulose esters.

When cotton is treated with nitric acid, the cellulose transforms into cellulose nitrate:

$$\left[C_6H_7O_2(OH)_3\right]_n + n\,HNO_3 \rightarrow \left[C_6H_7O_2\begin{matrix}OH\\OH\\ONO_2\end{matrix}\right]_n + n\,H_2O$$

Cellulose mononitrate

$$\left[C_6H_7O_2(OH)_3\right]_n + 2n\,HNO_3 \rightarrow \left[C_6H_7O_2\begin{matrix}OH\\ONO_2\\ONO_2\end{matrix}\right]_n + 2n\,H_2O$$

Cellulose dinitrate

$$\left[C_6H_7O_2(OH)_3\right]_n + 3n\,HNO_3 \rightarrow \left[C_6H_7O_2\begin{matrix}ONO_2\\ONO_2\\ONO_2\end{matrix}\right]_n + 3n\,H_2O$$

Cellulose trinitrate

A mixture of cellulose mono- and dinitrates is used in the manufacture of collodion wool.

The trinitrate, or pyroxylin, is employed as an explosive and in the production of smokeless gunpowder, in the manufacture of some nitrolacquers, and also of artificial leather.

Cellulose goes to produce cellulose acetate, which is a thermoplastic polymer. Cellulose diacetate $[C_6H_8O_3(CH_3COO)_2]_n$ is used to produce artificial silk (acetate rayon). Cellulose acetate is used in the production of lacquers.

Questions and Problems

1. How can the following transformations be performed:

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{Ethanol}}{C_2H_5OH}$$

How can the substances formed in the early stage of the transformations be detected?

2. In what respects are the properties of saccharose, starch, and cellulose similar? Why?

3. List the fields of application of cellulose and explain why starch cannot be used for the same purposes.

4. Write the equation of cellulose nitration and recall what other organic substances can be nitrated. Write the equation of the reaction and compare the structure and properties.

SUMMARY

An important class of natural compounds formally corresponding to the general formula $C_mH_{2n}O_n$ bears the name of carbohydrates. They are divided into two groups—simple carbohydrates (monosaccharides or monoses) and complex ones (polysaccharides or polyoses). Monosaccharides are polyatomic aldehyde- or ketone-alcohols that are related by mutual transformations to their cyclic polyacetal forms. The cyclic forms of the monosaccharides form as a result of the reaction of the carbonyl group with one of the alcohol hydroxyls within the same molecule (most frequently at the fourth or fifth carbon atom). This reaction forms an intramolecular hemiacetal.

Polysaccharides consist of monosaccharide residues bonded to one another by a glycoside bond. This group of carbohydrates includes low-molecular (sugar-like) polysaccharides containing from 2 to 10 monose residues, and high-molecular ones consisting of from scores to several tens of thousands of monose residues.

Glucose is one of the most widespread aldohexoses. The oxidation of glucose yields gluconic acid, while its reduction yields the hexatomic alcohol sorbitol. When the acyclic form converts to a cyclic hemiacetal one, a hemiacetyl hydroxyl forms at the first carbon atom. This hydroxyl differs in its properties from an alcohol hydroxyl.

The cyclic forms of monosaccharides differ from one another in the ring size: a six-membered ring is called a pyranose one, and a five-membered ring—a furanose one. The hemiacetal hydroxyl can occupy different positions relative to the ring plane, and in this connection two anomeric forms are distinguished, namely, α- and β-anomers.

Two monosaccharides combine to form a disaccharide. Saccharose consists of glucose and fructose.

Starch contains α-glucose residues, while cellulose contains β-glucose ones.

APPENDICES

1. Rounded off Values of Relative Atomic Masses (Atomic Weights) of Selected Chemical Elements

Element	Symbol	A_r	Element	Symbol	A_r	Element	Symbol	A_r
Aluminium	Al	27	Hafnium	Hf	178.5	Potassium	K	39
Antimony	Sb	122	Helium	He	4	Rubidium	Rb	85.5
Argon	Ar	40	Hydrogen	H	1	Scandium	Sc	45
Arsenic	As	75	Indium	In	115	Selenium	Se	79
Barium	Ba	137	Iodine	I	127	Silicon	Si	28
Beryllium	Be	9	Iron	Fe	56	Silver	Ag	108
Bismuth	Bi	209	Krypton	Kr	84	Sodium	Na	23
Boron	B	11	Lanthanum	La	139	Strontium	Sr	88
Bromine	Br	80	Lead	Pb	207	Sulphur	S	32
Cadmium	Cd	112	Lithium	Li	7	Tantalum	Ta	181
Calcium	Ca	40	Magnesium	Mg	24	Tellurium	Te	128
Carbon	C	12	Manganese	Mn	55	Thallium	Tl	204
Cesium	Cs	133	Mercury	Hg	201	Tin	Sn	119
Chlorine	Cl	35.5	Molybdenum	Mo	96	Titanium	Ti	48
Chromium	Cr	52	Neon	Ne	20	Tungsten	W	184
Cobalt	Co	59	Nickel	Ni	59	Uranium	U	238
Copper	Cu	64	Niobium	Nb	93	Vanadium	V	51
Fluorine	F	19	Nitrogen	N	14	Xenon	Xe	131
Gallium	Ga	70	Oxygen	O	16	Yttrium	Y	89
Germanium	Ge	73	Phosphorus	P	31	Zinc	Zn	65
Gold	Au	197	Platinum	Pt	195	Zirconium	Zr	91

2. Selected Important Physical Constants

Charge of electron	$1.602\,189\,2(46) \times 10^{-19}$ C
Rest mass of electron	$1.109\,534(47) \times 10^{-31}$ kg
Rest mass of proton	$1.672\,648\,5(86) \times 10^{-27}$ kg
Atomic mass unit	$1.660\,565\,5(86) \times 10^{-27}$ kg
Avogadro's constant	$6.022\,045(31) \times 10^{23}$ mol^{-1}
Molar gas constant	8.314 41(26) J·mol^{-1} K^{-1}
Faraday's constant	$9.648\,456(27) \times 10^{4}$ C·mol^{-1}
Absolute zero of temperature	−273.15° C
Standard atmosphere	101 325 Pa
Standard molar volume of ideal gas at STP (temperature of 0° C and pressure of 101 325 Pa)	$22.413\,83 \times 10^{-3}$ m^3·mol^{-1}

3. Solubility of Acids, Bases, and Salts in Water

Anions	Cations																		
	H^+	K^+	Na^+	NH_4^+	Ba^{2+}	Ca^{2+}	Mg^{2+}	Al^{3+}	Cr^{2+}	Fe^{2+}	Fe^{3+}	Ni^{2+}	Mn^{2+}	Zn^{2+}	Ag^+	Hg^+	Hg^{2+}	Pb^{2+}	Sn^{2+}	Cu^{2+}
OH^-		s	s	v	s	sp	in	in	in	in	in	in	in	in	—	—	—	in	in	in
Cl^-	s	s	s	s	s	s	s	s	s	s	s	s	s	s	in	in	s	sp°	s	s
Br^-	s	s	s	s	s	s	s	s	s	s	s	s	s	s	in	in	sp	sp°	s	s
I^-	s	s	s	s	s	s	s	s	s	s	h	s	s	s	in	in	in	in°	sp	—
S^{2-}	v	s	s	s	s	sp	sp	h	h	in	in	in	in	in	in	in	in	in	in	in
SO_3^{2-}	v	s	s	s	in	in	in	—	—	in	—	in	in	in	in	—	—	in	—	in
SO_4^{2-}	s	s	s	s	in	sp	s	s	s	s	s	s	s	s	sp	sp	s	in	s	s
PO_4^{3-}	s	s	s	s	in	in	in	in	in	in	in	in	in	in	in	in	in	in	in	in
CO_3^{2-}	v	s	s	s	in	in	in	—	—	in	—	in	in	in	in	in	—	in	h	h
SiO_3^{2-}	in	s	s	—	in	in	h	h	h	h	h	h	h	h	—	—	—	h	h	h
NO_3^-	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	h	s
CH_3COO^-	s	s	s	s	s	s	s	sp	s	s	s	s	s	s	s	sp	s	s	s	s

Note. Find the solubility of a compound at the intersection of the line containing its anion and the column containing its cation.
Symbols: s = soluble; sp = sparingly soluble; in = insoluble; h — the substance cannot be obtained in a solution owing to hydrolysis; v — the substance is volatile or decomposes with the formation of a gas; a dash signifies that the substance has not been obtained to date; the superscript "°" on a symbol indicates that the solubility of the substance increases when the solution is heated.

4. Dissociation Constants of Selected Weak Electrolytes in Aqueous Solutions at 25° C

Electrolyte	Formula	Dissociation constant
Acetic acid	CH_3COOH	2×10^{-5}
Aqueous ammonia solution	$NH_3 \cdot H_2O$	2×10^{-5}
Carbonic acid	H_2CO_3	$K_1 = 4.5 \times 10^{-7}$; $K_2 = 4.7 \times 10^{-11}$
Hydrocyanic acid	HCN	7.9×10^{-10}
Hydrofluoric acid	HF	6.6×10^{-14}
Hydrosulphuric acid	H_2S	$K_1 = 6 \times 10^{-8}$; $K_2 = 1 \times 10^{-14}$
Nitrous acid	HNO_2	4×10^{-4}
Phosphoric acid	H_3PO_4	$K_1 = 7.5 \times 10^{-3}$; $K_2 = 6.3 \times 10^{-8}$
Silicic acid	H_2SiO_3	$K_1 \approx 1 \times 10^{-10}$; $K_2 \approx 1 \times 10^{-22}$
Sulphurous acid	H_2SO_3	$K_1 = 1.6 \times 10^{-2}$; $K_2 = 6.3 \times 10^{-8}$

5. Dissociation Constants of Bases

Name	Formula	t, °C	K_b	pK_b
Aluminium hydroxide	$Al(OH)_3$	25	(III)1.38×10^{-9}	8.86
Ammonium hydroxide:				
apparent constant	NH_4OH	25	1.79×10^{-5}	4.75
true constant	NH_4OH	25	6.3×10^{-5}	4.20
Barium hydroxide	$Ba(OH)_2$	25	(II)2.3×10^{-1}	0.64
Cadmium hydroxide	$Cd(OH)_2$	30	(II)5.0×10^{-3}	2.30
Calcium hydroxide	$Ca(OH)_2$	25	(II)4.3×10^{-2}	1.37
Chromium hydroxide	$Cr(OH)_3$	26	(III)1.02×10^{-10}	9.99
Copper(II) hydroxide	$Cu(OH)_2$	25	(II)3.4×10^{-7}	6.67
Iron(II) hydroxide	$Fe(OH)_2$	25	(II)1.3×10^{-4}	3.89
Iron(III) hydroxide	$Fe(OH)_3$	25	(III)1.82×10^{-11}	10.74
Lead hydroxide	$Pb(OH)_2$	25	(I)9.6×10^{-4}	3.02
Magnesium hydroxide	$Mg(OH)_2$	25	(II)2.5×10^{-3}	2.60
Manganese hydroxide	$Mn(OH)_2$	30	(II)5.0×10^{-4}	3.30
Mercury(II) hydroxide	$Hg(OH)_2$	25	(I)4.0×10^{-12}	11.40
Nickel hydroxide	$Ni(OH)_2$	30	(II)2.5×10^{-5}	4.60
Silver hydroxide	AgOH	25	1.1×10^{-4}	3.96
Sodium hydroxide	NaOH	25	5.9	−0.77
Zinc hydroxide	$Zn(OH)_2$	25	(II)4×10^{-5}	4.40

6. Dissociation Constants of Inorganic Acids

Name	Formula	t, °C	K_a	pK_a
Aluminic	$HAlO_2$	18	4×10^{-13}	12.4
Arsenic (*ortho*)	H_3AsO_4	25	(I)5.98×10^{-3}	2.22
		25	(II)1.05×10^{-7}	6.98
		18	(III)3.89×10^{-12}	11.41
Boric	H_3BO_3	25	(I)5.8×10^{-10}	9.4
		20	(II)1.8×10^{-13}	12.74
		20	(III)1.6×10^{-14}	13.80
Bromic	$HBrO_3$	18	2×10^{-1}	0.7
Carbonic (apparent constants)	H_2CO_3	25	(I)4.45×10^{-7}	6.35
		25	(II)4.69×10^{-11}	10.33
Chromic	H_2CrO_4	25	(I)1×10	−1.0
		25	(II)3.16×10^{-7}	6.5
Hydrobromic	HBr	25	1×10^{9}	−9.0
Hydrochloric	HCl	25	1×10^{7}	−7.0
Hydrocyanic	HCN	25	7.9×10^{-10}	9.1
Hydrofluoric	HF	25	6.61×10^{-4}	3.18
Hydroiodic	HI	25	1×10^{11}	−11.0
Hydrosulphuric	H_2S	25	(I)6×10^{-8}	7.2
		25	(II)1×10^{-14}	14.0
Iodic	HIO_3	18	1.9×10^{-1}	0.72
		25	1.7×10^{-1}	0.77
Nitric	HNO_3	25	4.36×10	−1.64
Nitrous	HNO_2	18	4×10^{-4}	3.4
Phosphoric (*ortho*)	H_3PO_4	25	(I)7.5×10^{-3}	2.12
		25	(II)6.31×10^{-8}	7.20
		25	(III)1.26×10^{-12}	11.9
Phosphorous (*ortho*)	H_3PO_3	25	(I)1.6×10^{-2}	1.80
		25	(II)6.3×10^{-7}	6.2
Pyrophosphoric	$H_4P_2O_7$	18	(I)1.4×10^{-1}	0.85
		25	(II)1.1×10^{-2}	1.95
		25	(III)2.1×10^{-7}	6.68
		25	(IV)4.1×10^{-10}	9.39
Silicic (*meta*)	H_2SiO_3	18	(I)2.2×10^{-10}	9.66
		18	(II)1.6×10^{-12}	11.80
Sulphuric	H_2SO_4	25	(I)1×10^{3}	−3.0
		25	(II)1.2×10^{-2}	1.9
Sulphurous	H_2SO_3	25	(I)1.58×10^{-2}	1.8
		25	(II)6.31×10^{-8}	7.2

7. Dissociation Constants of Organic Acids at 25° C

Name	Formula	K_a	pK_a
Acetic	CH_3COOH	1.75×10^{-5}	4.75
Adipic	$CH_2—CH_2—COOH$	(I)3.8×10^{-5}	4.42
	$CH_2—CH_2—COOH$	(II)5.2×10^{-6}	5.28
m-Aminobenzoic	*m*-$H_2N—C_6H_4COOH$	1.8×10^{-5}	4.74
p-Aminobenzoic	*p*-$H_2N—C_6H_4COOH$	1.4×10^{-5}	4.85
Benzenesulphonic	$C_6H_5SO_3H$	2×10^{-1}	0.7
Benzoic	C_6H_5COOH	6.6×10^{-5}	4.18
o-Bromobenzoic	*o*-$Br—C_6H_4COOH$	1.4×10^{-3}	2.85
Butyric	$CH_3(CH_2)_2COOH$	1.52×10^{-5}	4.82
Formic	$HCOOH$	1.77×10^{-4}	3.75
Glycin (amino acetic)	H_2NCH_2COOH	1.3×10^{-10}	9.88
Lactic	$CH_3CH(OH)COOH$	1.37×10^{-4}	3.86
Oxalic	$HOOCCOOH$	(I)5.4×10^{-2}	1.27
		(II)5.4×10^{-5}	4.27
Phenol	C_6H_5OH	1.0×10^{-10}	10.0
Propionic	CH_3CH_2COOH	1.34×10^{-5}	4.87
Salicylic	*o*-HOC_6H_4COOH	(I)1.0×10^{-3}	3.00
		(II)1.5×10^{-14}	13.82
Valeric	$CH_3(CH_2)_3COOH$	1.4×10^{-5}	4.86

8. Standard Oxidation-Reduction Potentials

Element	Oxidized form	Electrons	Reduced form	Potential, V
Ag	Ag^+	$+e$	Ag	+0.799
Al	Al^{3+}	$+3e$	Al	−1.66
As	$H_3AsO_4 + 2H^+$	$+2e$	$HAsO_2 + 2H_2O$	+0.56
Au	Au^{3+}	$+3e$	Au	+1.50
	Au^+	$+e$	Au	+1.68
Ba	Ba^{2+}	$+2e$	Ba	−2.90
Bi	$BiO^+ + 2H^+$	$+3e$	$Bi + H_2O$	+0.32
Br	Br_2	$+2e$	$2Br^-$	+1.087
	$BrO_3 + 6H^+$	$+6e$	$Br^- + 3H_2O$	+1.45
Ca	Ca^{2+}	$+2e$	Ca	−2.79
Cd	Cd^{2+}	$+2e$	Cd	−0.403
Ce	Ce^{4+}	$+e$	Ce^{3+}	+1.44
Cl	Cl_2	$+2e$	$2Cl^-$	+1.359
	$ClO^- + H_2O$	$+2e$	$Cl^- + 2OH^-$	+0.88
	$ClO_2^- + H_2O$	$+2e$	$ClO^- + 2OH^-$	+0.66
	$ClO_3^- + 6H^+$	$+6e$	$Cl^- + 3H_2O$	+1.45
	$ClO_4^- + 2H^+$	$+2e$	$ClO_3^- + H_2O$	+1.19
Co	Co^{3+}	$+e$	Co^{2+}	+1.95
	Co^{2+}	$+2e$	Co	−0.28

Table 8 (continued)

Element	Oxidized form	Electrons	Reduced form	Potential, V
Cr	Cr^{3+}	$+e$	Cr^{2+}	−0.41
	Cr^{3+}	$+3e$	Cr	−0.74
	$CrO_2^- + 2H_2O$	$+3e$	$Cr + 4OH^-$	−1.20
	$Cr_2O_7^{2-} + 14H^+$	$+6e$	$2Cr^{3+} + 7H_2O$	+1.33
Cu	Cu^{2+}	$+2e$	Cu	+0.337
	Cu^+	$+e$	Cu	+0.531
	Cu^{2+}	$+e$	Cu^+	+0.159
Fe	Fe^{3+}	$+e$	Fe^{2+}	+0.771
	Fe^{3+}	$+3e$	Fe	−0.036
	Fe^{2+}	$+2e$	Fe	−0.440
	$Fe(C_{12}H_8N_2)_3^{3+}$	$+e$	$Fe(C_{12}H_8N_2)_3^{2+}$	+1.06
	Fe_3O_4	$+8e$	$3Fe + 4H_2O$	−0.085
H	$2H^+$	$+2e$	H_2	±0.0000
	H_2	$+2e$	$2H^+$	−2.25
	$H_2O_2 + 2H^+$	$+2e$	$2H_2O$	+1.77
Hg	$2Hg^{2+}$	$+2e$	Hg_2^{2+}	+0.907
	Hg^{2+}	$+2e$	Hg	+0.854
	Hg_2^{2+}	$+2e$	Hg	+0.792
	Hg_2Cl_2	$+2e$	$2Hg + 2Cl^-$	+0.268
I	I_2	$+2e$	$2I^-$	+0.536
	I_3^-	$+2e$	$3I^-$	+0.545
	$2HIO + 2H^+$	$+2e$	$I_2 + 2H_2O$	+1.45
	$IO_3^- + 5H^+$	$+4e$	$HIO + 2H_2O$	+1.14
	$IO_3^- + 6H^+$	$+6e$	$I^- + 3H_2O$	+1.08
K	K^+	$+e$	K	−2.92
Mg	Mg^{2+}	$+2e$	Mg	−2.37
Mn	Mn^{3+}	$+e$	Mn^{2+}	+1.51
	Mn^{2+}	$+2e$	Mn	−1.18
	$MnO_2 + 4H^+$	$+2e$	Mn^{2+}	+1.23
	$MnO_4^{2-} + 2H_2O$	$+2e$	$MnO_2 + 4OH^-$	+0.60
	MnO_4^-	$+e$	MnO_4^{2-}	+0.56
	$MnO_4^- + 4H^+$	$+3e$	$MnO_2 + 2H_2O$	+1.69
	$MnO_4^- + 8H^+$	$+5e$	$Mn^{2+} + 4H_2O$	+1.51
Mo	$H_2MoO_4 + 6H^+$	$+6e$	$Mo + 4H_2O$	0.0
	$MoO_4^{2-} + 4H_2O$	$+6e$	$Mo + 8OH^-$	−1.05
N	$NO_2^- + H_2O$	$+e$	$NO + 2OH^-$	−0.46
	$NO_3^- + 3H^+$	$+2e$	$HNO_2 + H_2O$	+0.94
	$NO_3^- + 2H^+$	$+e$	$NO_2 + H_2O$	+0.80
	$NO_3^- + 4H^+$	$+3e$	$NO + 2H_2O$	+0.96
	$NO_3^- + 8H^+$	$+6e$	$(NH_2OH)^+ + 2H_2O$	+0.73
	$NO_3^- + 10H^+$	$+8e$	$NH_4^+ + 3H_2O$	+0.87
Na	Na^+	$+e$	Na	−2.71
Ni	Ni^{2+}	$+2e$	Ni	−0.22
O	$O_2 + 4H^+$	$+4e$	$2H_2O$	+1.229
	$O_2 + 2H_2O$	$+4e$	$4OH^-$	+0.401

Table 8 (concluded)

Element	Oxidized form	Electrons	Reduced form	Potential, V
	$O_2 + 2H^+$	$+2e$	H_2O_2	+0.682
	$H_2O_2 + 2H^+$	$+2e$	$2H_2O$	+1.77
	$O_3 + 2H^+$	$+2e$	$O_2 + H_2O$	+2.07
P	$P + 3H^+$	$+3e$	PH_3	+0.06
	$P + 3H_2O$	$+3e$	$PH_3 + 3OH^-$	−0.89
	$H_3PO_2 + H^+$	$+e$	$P + 2H_2O$	−0.51
	$H_2PO_2^-$	$+e$	$P + 2OH^-$	−2.05
	$H_3PO_3 + 2H^+$	$+2e$	$H_3PO_2 + H_2O$	−0.50
	$H_3PO_4 + 2H^+$	$+2e$	$H_3PO_3 + H_2O$	−0.276
	$H_4P_2O_6 + 2H^+$	$+2e$	$2H_3PO_3$	+0.38
Pb	Pb^{2+}	$+2e$	Pb	−0.126
	Pb^{4+}	$+2e$	Pb^{2+}	+1.66
	$PbO_2 + 4H^+$	$+2e$	$Pb^{2+} + 2H_2O$	+1.455
S	S	$+2e$	S^{2-}	−0,48
	$S_4O_6^{2-}$	$+4e$	$2S_2O_3$	+0.09
	$S_2O_3^{2-} + 6H^+$	$+2e$	$2S + 3H_2O$	+0.5
	$SO_4^{2-} + 4H^+$	$+2e$	$H_2SO_3 + H_2O$	+0.17
	$S_2O_8^{2-}$	$+2e$	$2SO_4^{2-}$	+2.00
Sb	$Sb + 3H^+$	$+3e$	SbH_3	−0.51
	$SbO_2^- + 2H_2O$	$+3e$	$Sb + 4OH^-$	−0.675
	$SbO_3^- + H_2O$	$+2e$	$SbO_2^- + 2OH^-$	−0.43
Si	$Si + 4H^+$	$+4e$	SiH_4	−0.10
	$Si + 4H_2O$	$+4e$	$SiH_4 + 4OH^-$	−0.73
	$[SiF_6]^{2-}$	$+4e$	$Si + 6F^-$	−1.2
	$H_2SiO_3 + 4H^+$	$+4e$	$Si + 3H_2O$	−0.79
Sn	Sn^{2+}	$+2e$	Sn	−0.140
	Sn^{4+}	$+2e$	Sn^{2+}	+0.15
	$HSnO_2^- + H_2O$	$+2e$	$Sn + 3OH^-$	−0.91
	$Sn(OH)_6$	$+2e$	$HSnO_2^- + 3OH^- + H_2O$	−0.93
Sr	Sr^{2+}	$+2e$	Sr	−2.89
Ti	Ti^{2+}	$+2e$	Ti	−1.63
	$TiO^{2+} + 2H^+$	$+e$	$Ti^{3+} + H_2O$	+0.1
	Ti^{3+}	$+e$	Ti^{2+}	−0.37
	Ti^{4+}	$+e$	Ti^{3+}	+0.092
Zn	Zn^{2+}	$+2e$	Zn	−0.764
	$ZnO_2^{2-} + 2H_2O$	$+2e$	$Zn + 4OH^-$	−1.216

9. Electron Configuration of the Elements

Atomic number	Element	Shell															
		1	2		3			4				5			6		7
		K	*L*		*M*			*N*				*O*			*P*		*Q*
		Orbital															
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
1	Hydrogen	1																	
2	Helium	2																	
3	Lithium	2	1																
4	Beryllium	2	2																
5	Boron	2	2	1															
6	Carbon	2	2	2															
7	Nitrogen	2	2	3															
8	Oxygen	2	2	4															
9	Fluorine	2	2	5															
10	Neon	2	2	6															
11	Sodium	2	2	6	1														
12	Magnesium	2	2	6	2														
13	Aluminium	2	2	6	2	1													
14	Silicon	2	2	6	2	2													
15	Phosphorus	2	2	6	2	3													
16	Sulphur	2	2	6	2	4													
17	Chlorine	2	2	6	2	5													
18	Argon	2	2	6	2	6													
19	Potassium	2	2	6	2	6		1											
20	Calcium	2	2	6	2	6		2											
21	Scandium	2	2	6	2	6	1	2											
22	Titanium	2	2	6	2	6	2	2											
23	Vanadium	2	2	6	2	6	3	2											
24	Chromium	2	2	6	2	6	5	1											
25	Manganese	2	2	6	2	6	5	2											
26	Iron	2	2	6	2	6	6	2											
27	Cobalt	2	2	6	2	6	7	2											
28	Nickel	2	2	6	2	6	8	2											
29	Copper	2	2	6	2	6	10	1											
30	Zinc	2	2	6	2	6	10	2											
31	Gallium	2	2	6	2	6	10	2	1										
32	Germanium	2	2	6	2	6	10	2	2										
33	Arsenic	2	2	6	2	6	10	2	3										
34	Selenium	2	2	6	2	6	10	2	4										
35	Bromine	2	2	6	2	6	10	2	5										
36	Krypton	2	2	6	2	6	10	2	6										
37	Rubidium	2	8		18			2	6			1							
38	Strontium	2	8		18			2	6			2							

Table 9 (continued)

Atomic number	Element	Shell															
		1	2		3			4				5				6	7
		K	*L*		*M*			*N*				*O*				*P*	*Q*
		Orbital															
		1s	*2s*	*2p*	*3s*	*3p*	*3d*	*4s*	*4p*	*4d*	*4f*	*5s*	*5p*	*5d*	*5f*	*6s*	*6p*	*6d*	*7s*
39	Yttrium	2	8		18			2	6	1		2							
40	Zirconium	2	8		18			2	6	2		2							
41	Niobium	2	8		18			2	6	4		1							
42	Molybdenum	2	8		18			2	6	5		1							
43	Technetium	2	8		18			2	6	5		2							
44	Ruthenium	2	8		18			2	6	7		1							
45	Rhodium	2	8		18			2	6	8		1							
46	Palladium	2	8		18			2	6	10									
47	Silver	2	8		18			2	6	10		1							
48	Cadmium	2	8		18			2	6	10		2							
49	Indium	2	8		18			2	6	10		2	1						
50	Tin	2	8		18			2	6	10		2	2						
51	Antimony	2	8		18			2	6	10		2	3						
52	Tellurium	2	8		18			2	6	10		2	4						
53	Iodine	2	8		18			2	6	10		2	5						
54	Xenon	2	8		18			2	6	10		2	6						
55	Cesium	2	8		18			2	6	10		2	6			1			
56	Barium	2	8		18			2	6	10		2	6			2			
57	Lanthanum	2	8		18			2	6	10		2	6	1		2			
58	Cerium	2	8		18			2	6	10	2	2	6			2			
59	Praseodymium	2	8		18			2	6	10	3	2	6			2			
60	Neodymium	2	8		18			2	6	10	4	2	6			2			
61	Promethium	2	8		18			2	6	10	5	2	6			2			
62	Samarium	2	8		18			2	6	10	6	2	6			2			
63	Europium	2	8		18			2	6	10	7	2	6			2			
64	Gadolinium	2	8		18			2	6	10	7	2	6	1		2			
65	Terbium	2	8		18			2	6	10	9	2	6			2			
66	Dysprosium	2	8		18			2	6	10	10	2	6			2			
67	Holmium	2	8		18			2	6	10	11	2	6			2			
68	Erbium	2	8		18			2	6	10	12	2	6			2			
69	Thulium	2	8		18			2	6	10	13	2	6			2			
70	Ytterbium	2	8		18			2	6	10	14	2	6			2			
71	Lutetium	2	8		18			2	6	10	14	2	6	1		2			
72	Hafnium	2	8		18			2	6	10	14	2	6	2		2			
73	Tantalum	2	8		18				32			2	6	3		2			
74	Tungsten	2	8		18				32			2	6	4		2			
75	Rhenium	2	8		18				32			2	6	5		2			

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